

# **Chemistry Revision Themes**

## **Part II**

**Themes:**

**Chemical Equilibria**

**Chemical Energetics**

**Chemical Kinetics**

**Organic Chemistry I**

**Organic Chemistry II**

First Year (AS) Chemistry guide: ■      Second Year (A2) Chemistry guide: ■  
(NB: Consult *your* examining board syllabus to establish precise requirements)

## Part II:

### Theme Seven: Chemical Equilibria

42

Reversible reactions, Dynamic equilibrium, Examples of reversible reactions, Le Chatelier's principle, The equilibrium law,  $K_p$  & partial pressure, Degree of dissociation and mole fraction, Homogeneous & heterogeneous reactions.

### Theme Eight: Chemical Energetics

53

Exothermic & endothermic, Enthalpy change, Standard enthalpy of formation, Standard enthalpy of combustion, Enthalpy of neutralisation, Enthalpy of displacement, Cooling curve, Corrected temperature, Lavoisier & Laplace law, Hess's law, Reaction cycles, Bond enthalpy, Energy level diagrams, Lattice enthalpy, Born-Haber cycle, Solubility and enthalpy of solution, Chemical thermodynamics, Entropy and Free Energy.

### Theme Nine: Chemical Kinetics

69

Temperature effect, Collision theory, Activation energy, Transition state, Molecular orientation, Energy level diagrams, Maxwell-Boltzmann energy distribution curves, Concentration effect, Physical state effect, Catalytic effect, Types of catalyst, Thermodynamic & Kinetic stability, Rate equation, Reaction order, Monitoring change in concentration with time, Theoretical rate equations, The Arrhenius equation.

### Theme Ten: Organic Chemistry I

85

Organic compounds, Functional groups, Homologous series, Aliphatic compounds, Aromatic compounds, Benzene, Straight & Branched chain molecules, Saturated & Unsaturated compounds, Structural isomers, Electrophiles & Nucleophiles, Organic Nomenclature, The Alkanes, Fuels, The Alkenes, Geometrical isomers, Polymer applications, Naturally occurring alkenes.

### Theme Eleven: Organic Chemistry II

100

Halogenoalkanes - properties, reactions, uses, Saytzeff rule, Alcohols - properties & reactions, Naturally occurring hydroxy & halogen containing compounds, CFC's & Ozone layer, Use of Infra-red Spectroscopy to identify functional groups.

# Theme Seven

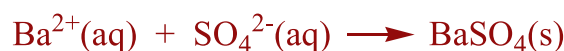
## Chemical Equilibria

This is concerned with the **yield** or extent of a chemical reaction and the factors which control this.

The English chemist W. Williamson (1850) was the first to properly study reversible reactions during his work on ethers.

The Norwegian chemists C. Guldberg & P. Waage (1860), and later, the American physicist J. Gibbs (1875) contributed greatly to our present understanding of chemical equilibria. The German chemist F.W. Ostwald (1887) finally put the subject on a proper footing.

Many of the inorganic reactions we study in the laboratory, at A-level, produce **good** yields of products.

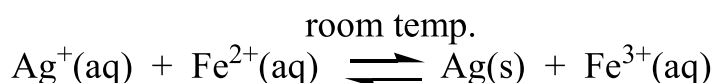


(You need to remember these reactions & equations. They are important in qualitative analysis.)

These reactants, mixed in stoichiometric proportions, provide 100% yield of products. The reactions are irreversible (ie, go one way, as indicated by the arrow).

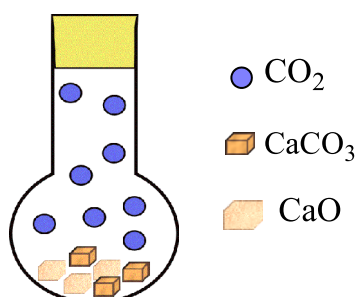
However, there are some reactions which occur to a *partial* extent and can go in **both** directions. In their chemical equations, we use double arrows (or double half arrows) to indicate this.

eg,



These reactions are **reversible**. The forward reactions (ie, left to right) and backward reactions (ie, right to left) are occurring together (at the same time).

In an enclosed reaction vessel, under constant conditions of temperature and pressure, the concentrations of the chemical species eventually attain steady states and we then say that the reacting systems are in **dynamic equilibrium**.



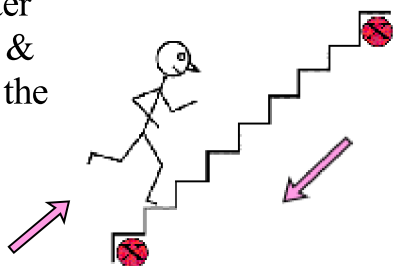
**Dynamic equilibrium**  
Forward and reverse reactions are occurring at the same rate and the proportions of the reactants remains unchanged.

## Chemical Equilibria

### An Analogy of Dynamic Equilibrium

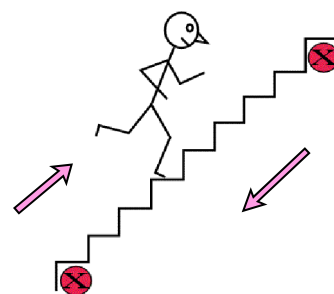
Here is a man, repeatedly, running *up* a *downward moving* escalator.

He is running faster than the escalator & eventually reaches the top.



In this second case, the man is running at the *same speed* as the escalator & stays, more or less, in the same position.

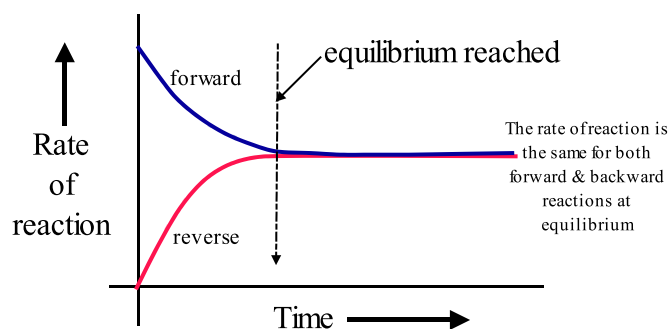
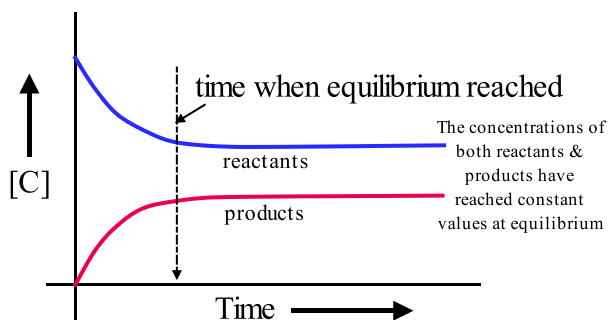
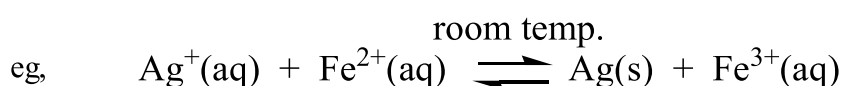
We could say that he & the escalator are in *dynamic equilibrium*!



This is only an analogy!

The thing to realise is that for reaction mixtures in dynamic equilibrium, the forward and backward reactions are still occurring but the concentrations of chemical species are constant because the rates of the two reactions are equal.

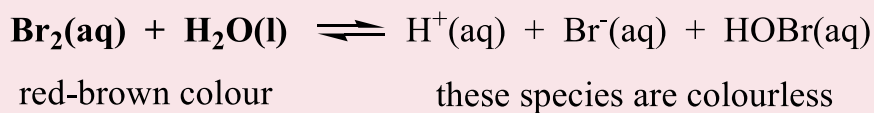
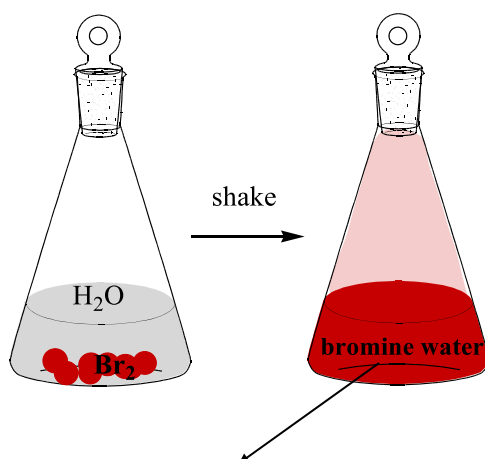
### Variations of concentrations and rates in reversible reactions:





## Further examples of reversible reactions and dynamic equilibrium

### Bromine Water



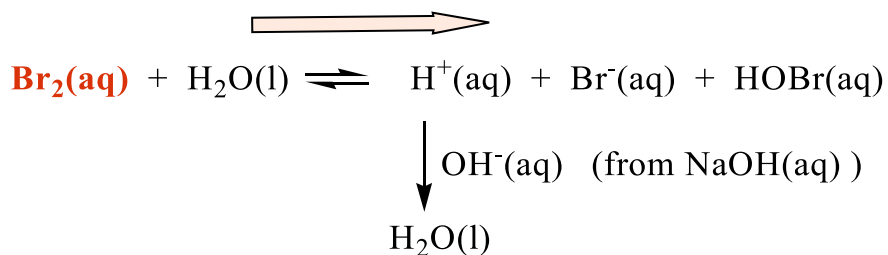
This equilibrium lies very much to the left.

### How to shift this equilibrium to the right?

Add sodium hydroxide solution.

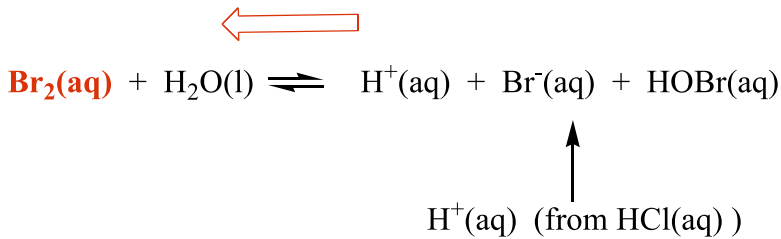
This removes hydrogen ion which causes bromine and water to react, generating more hydrogen ion and establishing a new equilibrium.

Since bromine is used up, the red-brown colour gradually disappears.



## Chemical Equilibria

Adding strong acid will reverse the equilibrium shift.



It is clear from this bromine-water example that altering the concentration of hydrogen ion shifts the position of equilibrium and changes the concentrations of the other reactants.

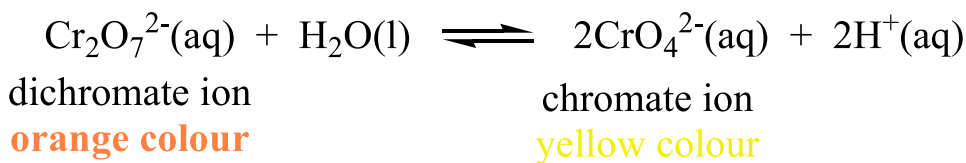
We can predict what is likely to occur in a situation like this by applying

## Le Chatelier's Principle (1888)

ie,

*when the conditions of a system in equilibrium are altered, the position of equilibrium changes in such a way as to try and restore the original conditions.*

Consider, **Dichromate solution**



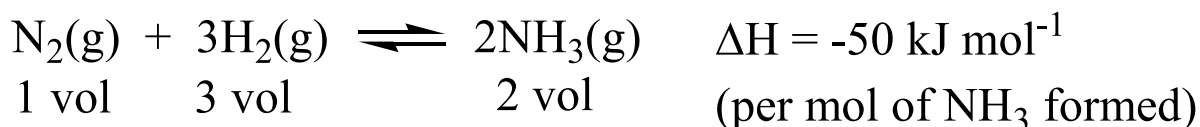
This equilibrium is established when potassium dichromate is dissolved in water to give a dilute solution. The solution is orange because the equilibrium lies to the left.

What will happen if dilute sodium hydroxide is added to the equilibrium mixture?

Hydroxide ion will remove hydrogen ion with the formation of water. Le Chatelier tells us that the system will respond to this by **replacing** the hydrogen ion. This is achieved by reacting dichromate ion with water and shifting the equilibrium to the right. A colour change is observed, from orange to yellow, as dichromate ion is used up and more chromate ion is formed.

### The Haber Process

Fritz Haber developed a process for manufacturing ammonia in 1913.



**What happens if the **temperature** of the equilibrium mixture is raised?**

The equilibrium will shift to the left (the endothermic direction). Heat content will be reduced. The concentration of ammonia will decrease and the concentrations of nitrogen & hydrogen will increase as the new equilibrium is established.

Reducing the temperature has the opposite effect.

**What happens if the **pressure** is changed by, for example, compressing the reaction mixture?**

This increases the number of molecules per unit volume. The equilibrium will shift in favour of fewer molecules, ie, shift to the right (more ammonia, less nitrogen & hydrogen).

#### Summary:

The formation of ammonia by the Haber Process is favoured by low temperatures and high pressures. At 200°C and 600 atm the yield of ammonia is about 95%.

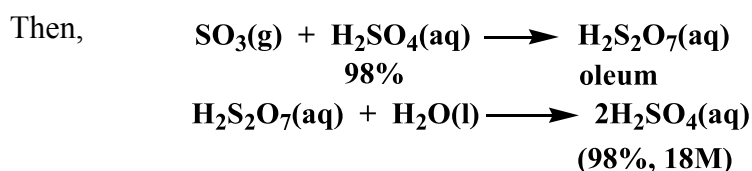
In practice, a temperature of about 500°C and a pressure of about 200 atm is used.

An iron catalyst is also employed. This helps speed up the reaction but, characteristic of catalysts, it does not affect the yield.

Under these conditions the conversion is about 15%; unreacted nitrogen and hydrogen are recycled.

### The Contact Process

This is a process for manufacturing sulphuric acid. It was patented in 1831 by Peregrine Phillips, a Bristol vinegar merchant. However, it was some time later before it was developed as a commercial process by Rudolf Knietsch working for the German chemical company [BASF](#) in 1888.

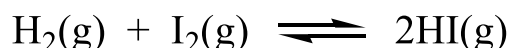


Le Chaterlier's principle predicts that high pressure and low temperature are required for a high yield of sulphur trioxide in the key reversible reaction.

Commercially, a pressure of just over 1 atm and a temperature of 450°C are found to be economically advantageous. Vanadium(V) oxide is the catalyst of choice.

### The Equilibrium Law

Consider the reversible reaction,



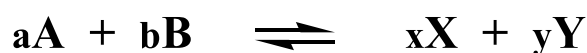
Experiments show that at a given temperature the following product/reactants ratio is constant.

$$\frac{[\text{HI}]^2}{[\text{H}_2] \times [\text{I}_2]} = \text{constant (K)}$$

K is known as the **equilibrium constant**. The symbol [ ] refers to concentration in moles per  $\text{dm}^3$ . For this particular reaction the value of K is 48.8 at a temperature of  $460^\circ\text{C}$ .

The Norwegian chemists **C.M. Guldberg & P. Waage** were the first to propose that for reversible reactions, like the one above, product/reactant ratios are always constant at a particular temperature.

ie, for the general case,



$$K_c = \frac{[\text{X}]^x \cdot [\text{Y}]^y}{[\text{A}]^a \cdot [\text{B}]^b}$$

Product concentrations always on the top of the expression

This equation is a statement of the **equilibrium law**.

Providing the temperature remains constant, a change in concentration of a reactant will induce changes in the concentrations of the other reactants so that the value of K remains constant.

Only changes in temperature will alter the value of K. If the forward reaction is **exothermic**, K will *decrease* with rise in temperature. If the forward reaction is **endothermic**, K will *increase* with rise in temperature

(This is predicted in Le Chatelier's principle (p 45) )

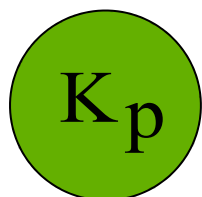
**NB:**

If  $K > 10^5$  then almost complete conversion to products.

If  $K < 10^{-5}$  then very very small conversion to products.

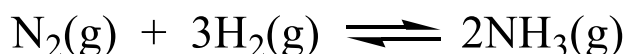
If  $K$  between 0.01 and 100 then reactants and products present in similar amounts at equilibrium.

$K$  does not indicate how fast a reaction proceeds, it indicates *yield*.



For reactions involving gases, *partial pressures* are often used in the equilibrium expressions instead of concentrations.

eg,



$$K_p = \frac{(\text{pNH}_3 \text{ atm})^2}{(\text{pN}_2 \text{ atm}) \cdot (\text{pH}_2 \text{ atm})^3}$$

at 450°C this has a value of  $4.34 \times 10^{-5} \text{ atm}^{-2}$

**Note:** the partial pressure of a gas is the pressure the gas would exert if it alone occupied the same volume as the gas mixture at the same temperature.

The sum of the partial pressures of the constituent gases equals the total pressure exerted by the mixture.

### Nitrogen(IV) oxide

At room temperature this gas has a reddish-brown colour (it is toxic & is a constituent of car exhaust gases). It readily dimerises. The dimer is a colourless crystalline solid at -10°C. At 50°C an equilibrium mixture exists containing 35% of the gaseous dimer.

ie,



At about 140°C the equilibrium mixture consists almost entirely of  $\text{NO}_2$ .

## Chemical Equilibria

For this reaction, what is the equilibrium expression in terms of partial pressures (based on the chemical equation given on p49)?

It is:

$$K_p = \frac{(p_{\text{NO}_2})^2}{(p_{\text{N}_2\text{O}_4})}$$

At 45°C  $p_{\text{NO}_2} = 105 \text{ kPa}$  and the total pressure of the mixture is 202.3 kPa.

What is the value of the equilibrium constant?

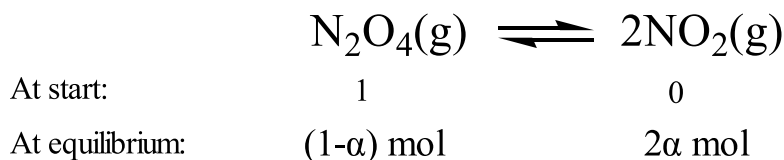
$$K_p = \frac{(105)^2}{(202.3 - 105)} = 113.3 \text{ kPa}$$

## Degree of dissociation and mole fraction?

Sticking with the above example, let the initial amount of dinitrogen tetroxide be 1 mole and suppose  $\alpha$  mole of this breaks up (dissociates) giving nitrogen dioxide molecules.

The amount,  $\alpha$ , is known as the *degree of dissociation*.

ie,



Total number of moles at equilibrium =  $1-\alpha + 2\alpha = 1+\alpha$

The ratios,  $(1-\alpha)/(1+\alpha)$  &  $2\alpha/(1+\alpha)$  are known as the *mole fractions* of reactants.

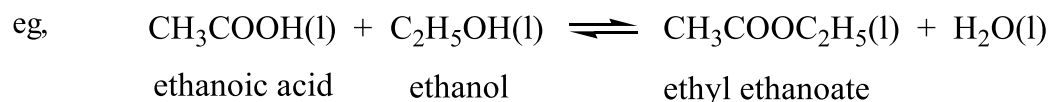
**partial pressure of a reactant = mole fraction x total pressure**

At a particular temperature and 101 kPa total pressure,  $\alpha = 0.50$ . What is the value of  $K_p$ ? Applying the expression for  $K_p$  at the top of the page,

$$K_p = \frac{(2\alpha/(1+\alpha) \times 101 \text{ kPa})^2}{((1-\alpha)/(1+\alpha) \times 101 \text{ kPa})} = \frac{4\alpha^2 \cdot 101}{1-\alpha^2} = 134.7 \text{ kPa}$$

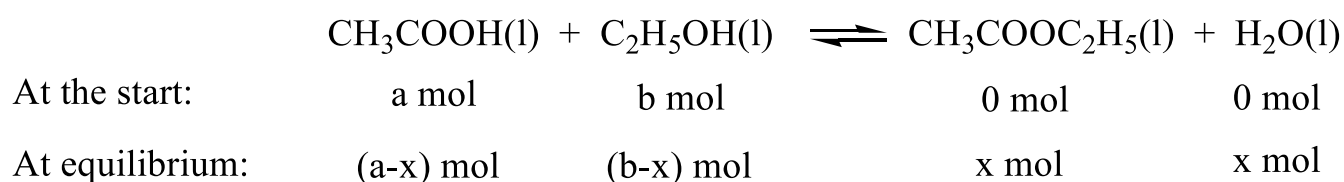
## Chemical Equilibria

### Homogeneous liquid phase equilibria



An equilibrium in which all the reactants are in a single liquid phase (homogeneous).

For this equilibrium at room temperature, 
$$K_c = \frac{[\text{ethyl ethanoate}] \cdot [\text{water}]}{[\text{ethanoic acid}] \cdot [\text{ethanol}]} = 4.0$$



(volume of mixture = V dm<sup>3</sup>)

$$K_c = \frac{x/V \cdot x/V}{(a-x)/V \cdot (b-x)/V} = \frac{x^2}{(a-x) \cdot (b-x)}$$

60g of ethanoic acid were heated with 46g of ethanol at 50°C until equilibrium was established. 12g of water and 58.7g of ethyl ethanoate were produced.  
 What is the value of  $K_c$ ?

Answer:

$$K_c = \frac{58.7/88 \cdot 12/18}{(60/60 - 12/18) \cdot (46/46 - 12/18)} = \frac{4/9}{1/3 \cdot 1/3} = 4.0$$

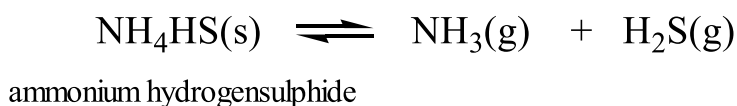
For this equilibrium  $K_c$  does not vary much with temperature.



## Chemical Equilibria

### Heterogeneous equilibria

eg,



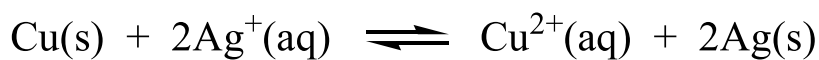
Experiments show that in a case like this, where solid is in equilibrium with gas, the equilibrium constant is independent of the amount of solid present at a given temperature.

So,

$$K_p = p\text{NH}_3 \cdot p\text{H}_2\text{S}$$

Displacement reactions,

eg,



$$K_c = \frac{[\text{Cu}^{2+}\text{(aq)}]}{[\text{Ag}^+\text{(aq)}]^2}$$

Liquid bromine in contact with gaseous bromine.



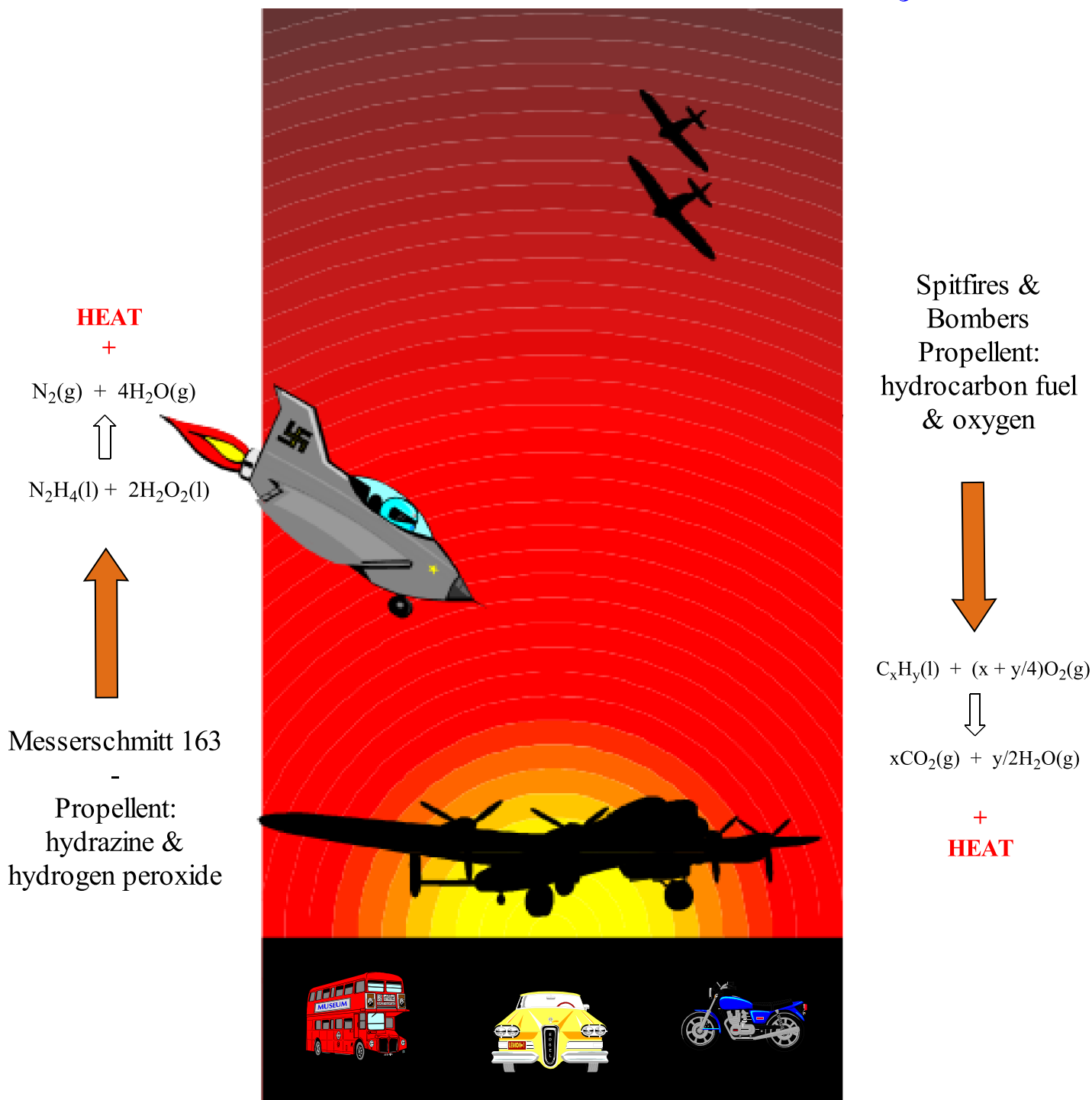
$$K_p = p\text{Br}_2$$

# Theme Eight

## Chemical Energetics

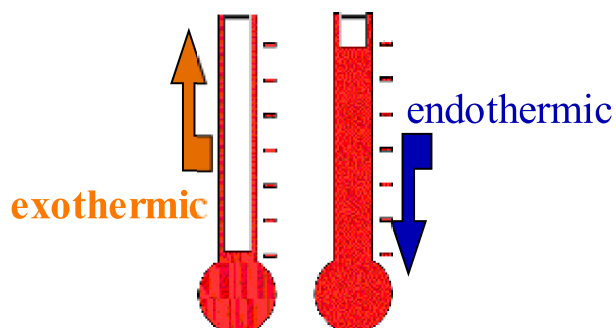
Hermann Ludwig Ferdinand von Helmholtz  
 Julius Robert von Mayer  
 James Prescott Joule  
 William Thomson  
 Peter Waage

Pierre Eugene Marcelin Berthelot  
 Rudolf Julius Emanuel Clausius  
 Nicolas Leonard Sadi Carnot  
 Otto Maximilian Guldberg  
 Gustin Henri Hess



## Chemical Energetics

Chemical reactions involve heat change. Usually heat is *liberated* to the surroundings and the reaction mixture and its container get warm. However, sometimes heat is *absorbed* from the surroundings and the mixture and its container get cold.



Temperature of reaction vessel

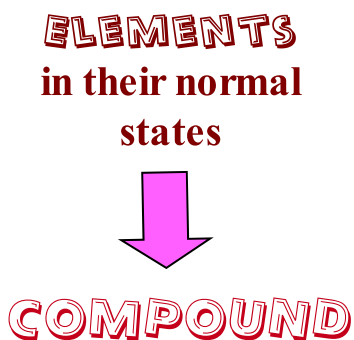
The symbol for heat change is  $\Delta H$  also known as *enthalpy change* from the Greek *enthalpy* meaning *warm*.  $\Delta H^\ominus$  is the symbol for *standard enthalpy change*, ie, measured at 1 atmosphere pressure and 25°C.

Eg,

$$\Delta H_f^\ominus$$

### standard enthalpy of formation

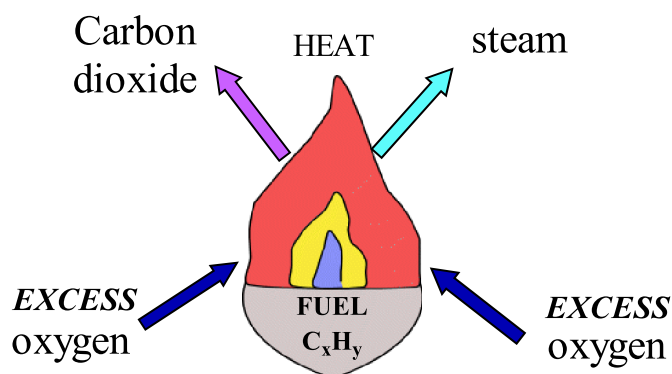
*The enthalpy change when one mole of a substance is synthesised from its elements under standard conditions (ie, 1 atmosphere pressure and 298K).*



$$\Delta H_c^\ominus$$

### standard enthalpy of combustion

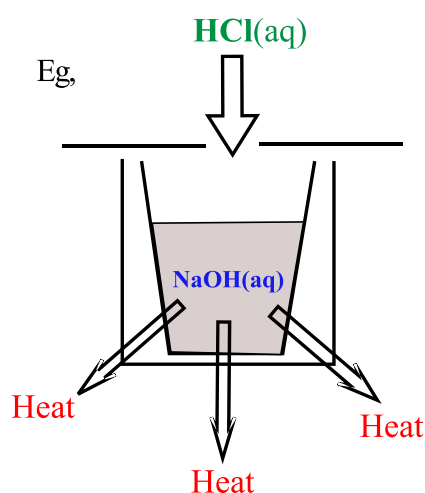
*The enthalpy change when one mole of a compound undergoes complete combustion in excess oxygen under standard conditions (ie, 1 atmosphere pressure and 298K).*



## Further examples of reactions involving heat change

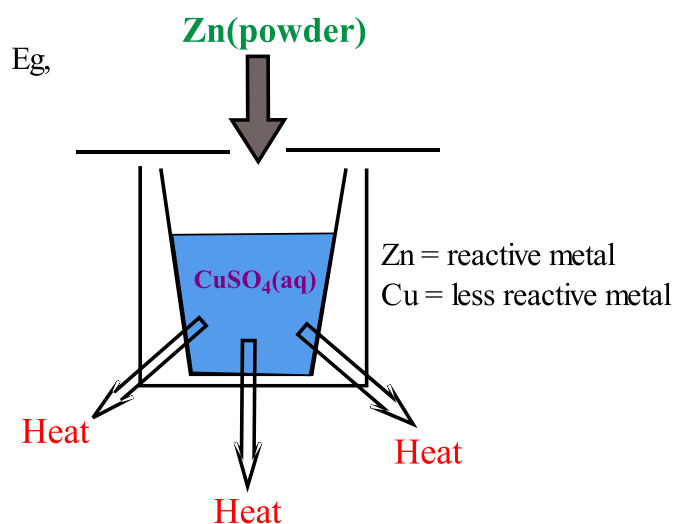
$$\Delta H^{\ominus}_{\text{neutr}}$$

The enthalpy change when a specified acid neutralises a specified base in dilute aqueous solution to form 1 mole of water under standard conditions.

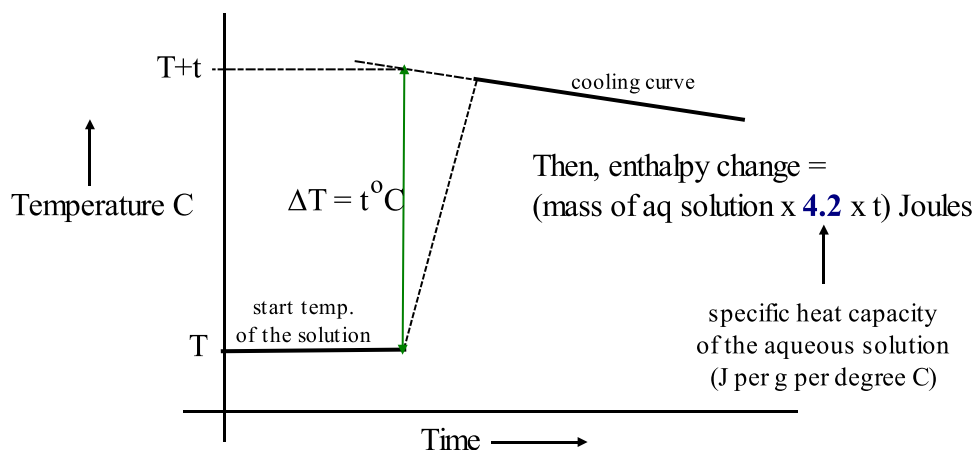


$$\Delta H^{\ominus}_{\text{displacement}}$$

The enthalpy change when an excess of a reactive metal displaces 1 mole of a less reactive metal from aqueous solution under standard conditions.



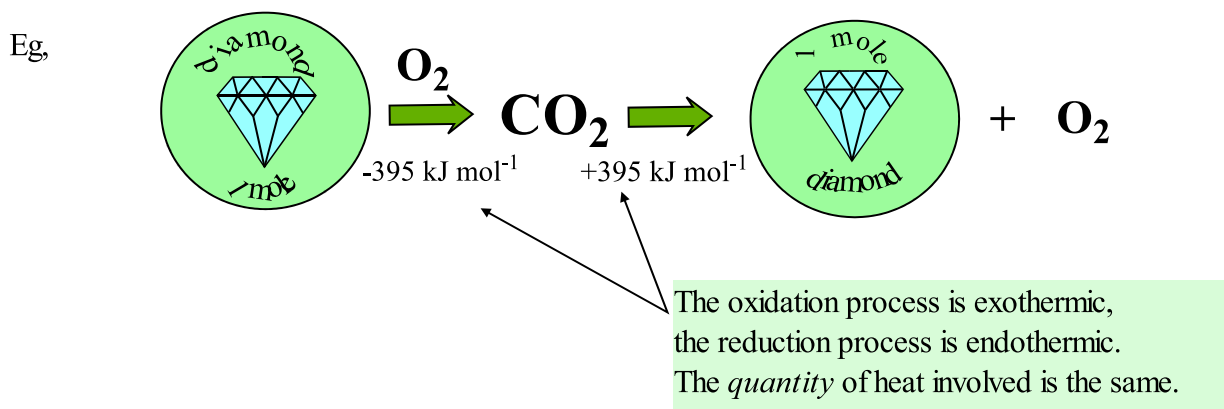
When measuring these enthalpy change values it is sometimes convenient to monitor the progress of the reaction by recording the temperature change with time. It is then possible to obtain a **corrected temperature** change which helps to compensate for heat loss from the calorimeter.



## Chemical Energetics

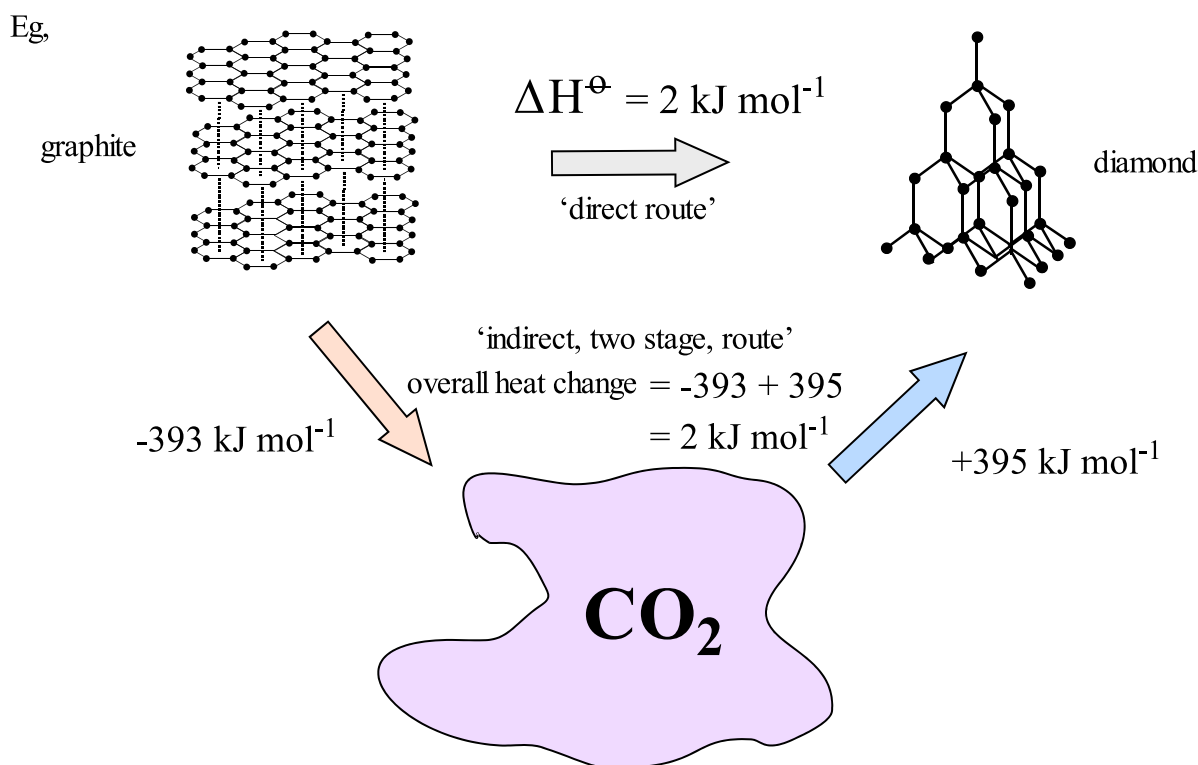
### Lavoiser & Laplace law (1780)

*The amount of heat emitted in a chemical reaction is equal to the amount of heat that would be absorbed if the reaction took place in the opposite direction.*



### Hess's law (law of constant heat summation 1840)

*The enthalpy change in a chemical reaction is the same whether the reaction takes place directly or in a number of stages.*



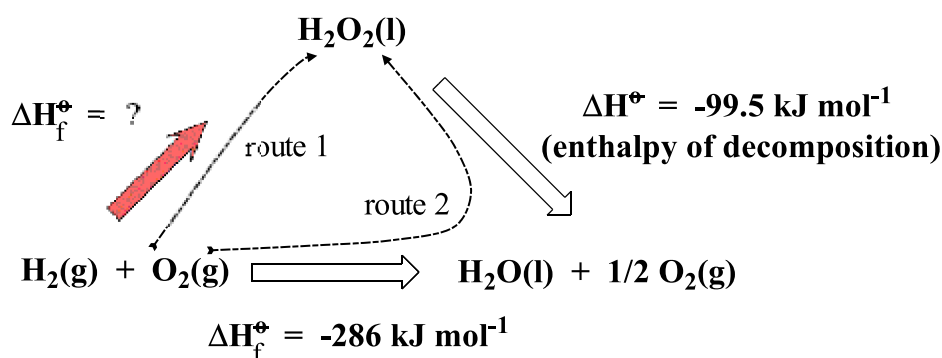
## Chemical Energetics

Another example:

If it was possible to convert hydrogen and oxygen *directly* into hydrogen peroxide, what would be the heat change per mole?

It can be calculated using **Hess's law** and readily available thermochemical data.

ie,



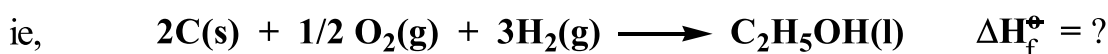
Equate routes 1 and 2:

$$\Delta H_f^\ominus = -286 + (+99.5) \quad \leftarrow \text{The reverse of the decomposition}$$

$$= -186.5 \text{ kJ mol}^{-1}$$

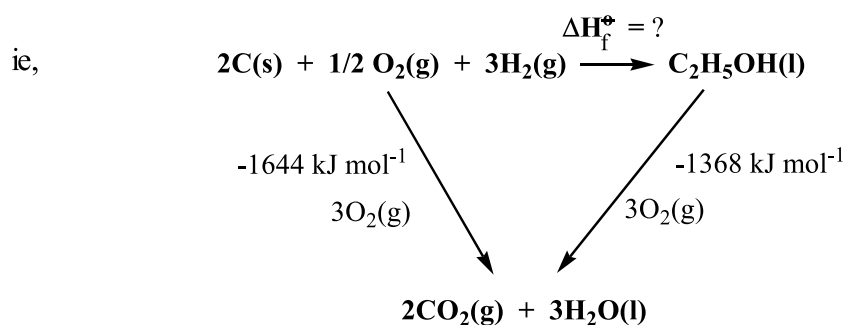
Since many **organic compounds** are difficult, if not impossible, to synthesise directly from their elements the above procedure is useful for determining their enthalpies of formation.

Suppose, for example, we require the enthalpy of formation of ethanol.



We can incorporate the formation reaction into a reaction cycle which also involves the combustion of ethanol.

(Enthalpy of combustion values are very useful in thermochemical calculations)



These combustion values can be measured in the laboratory or retrieved from the literature.

The standard enthalpy of combustion was defined on page 54.

Then applying Hess's law,

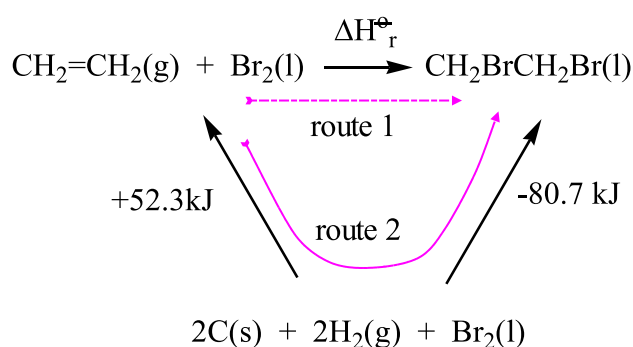
$$\Delta H_f^\ominus = (-1644) + (+1368) = -276 \text{ kJ mol}^{-1}$$

## Chemical Energetics

Having obtained and compiled a list of standard enthalpy of formation values, they can be used to calculate standard enthalpies of reaction.

eg, What is the enthalpy change when one mole of bromine ( $\text{Br}_2$ ) reacts completely with one mole of ethene to give one mole of 1,2-dibromoethane?

Using data from the literature (data books) and applying Hess's law:



$$\Delta H^\ominus_{\text{r}} = (-52.3) + (-80.7) = -133.0 \text{ kJ mol}^{-1}$$

From this calculation, and others like it, we can formulate a general rule:

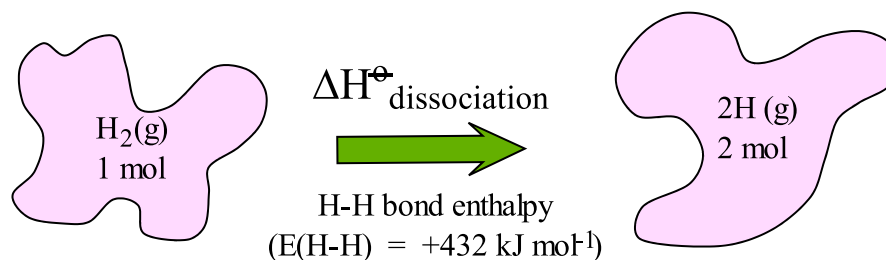
***The enthalpy of reaction =***  
***(the sum of the enthalpy of formation of the products) - (the sum of the enthalpy of formation of the reactants)***

$$\Delta H^\ominus_{\text{r}} = \sum \Delta H^\ominus_{\text{f}}(\text{products}) - \sum \Delta H^\ominus_{\text{f}}(\text{reactants})$$

**Bond Enthalpy (Energy)** is defined as:

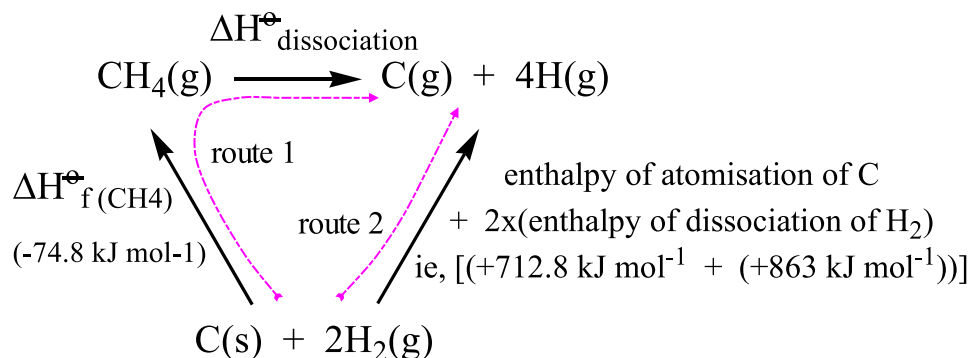
*The average enthalpy change on breaking one mole of a particular covalent bond when the process is carried out in the gas phase.*

eg,



## Chemical Energetics

The average C-H bond enthalpy can be deduced by constructing a reaction cycle involving methane:



Then, applying Hess's law:

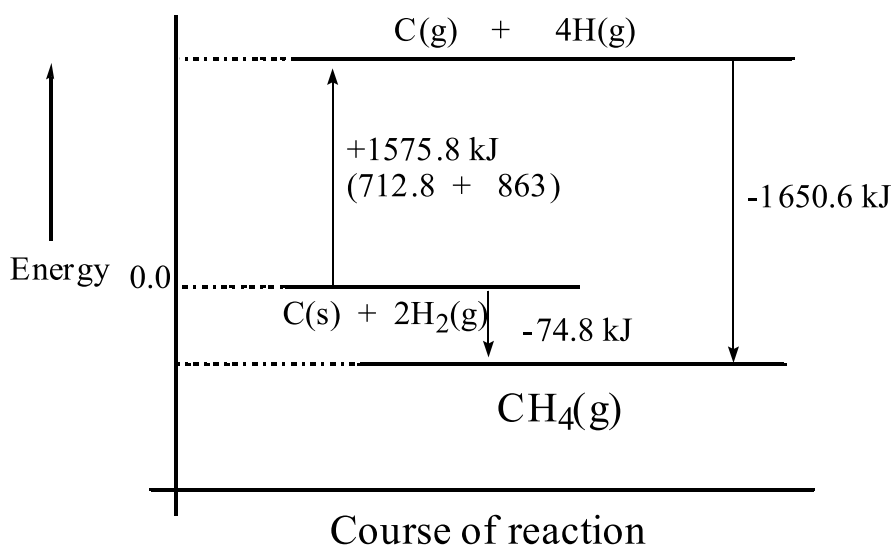
$$-74.8 + \Delta H^{\ominus}_{\text{dissoc'n}} = +712.8 + 863$$

$$\Delta H^{\ominus}_{\text{dissoc'n}} = 74.8 + 712.8 + 863 = 1650.6 \text{ kJ mol}^{-1}$$

Therefore, C-H bond enthalpy =  $1650.6/4 = 412.6 \text{ kJ mol}^{-1}$

This is known as the *average bond C-H bond energy* since it is the average dissociation energy of four C-H

This result can be represented on an energy level diagram.



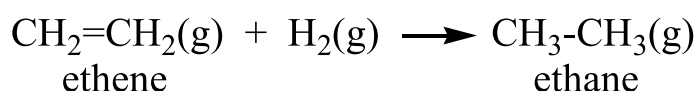


## Chemical Energetics

Bond enthalpies can be used to calculate *approximate* enthalpies of reaction:

$$\Delta H_r^\ominus = \sum \text{average bond enthalpies of reactants} - \sum \text{average bond enthalpies of products}$$

eg, Calculate the enthalpy of hydrogenation of ethene given,



Bond	Bond enthalpy (kJ mol <sup>-1</sup> )
H-H	+436
C-H	+413
C-C	+346
C=C	+611

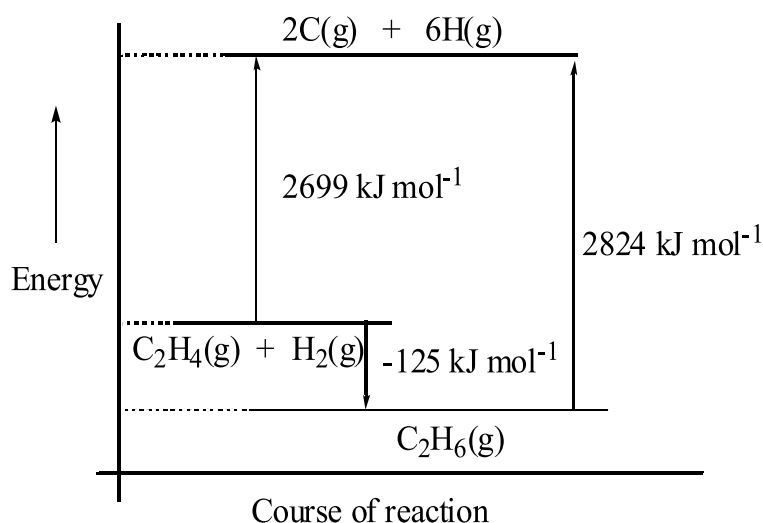
From the data,

sum of the bond energies of the **reactants** = 611 + (4x413) + 436 = 2699 kJ

Sum of the bond energies of the **products** = 346 + (6x413) = 2824 kJ

Enthalpy of hydrogenation = 2699 - 2824 = -125 kJ mol<sup>-1</sup>

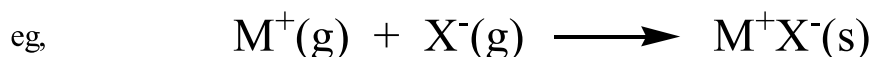
Finally we can construct the energy level diagram.



## Lattice Enthalpy

Lattice enthalpy may be defined as,

*The standard enthalpy change when 1 mole of a solid ionic compound is formed from its isolated gaseous ions.*



**The more exothermic this process is the more stable the ionic solid.**

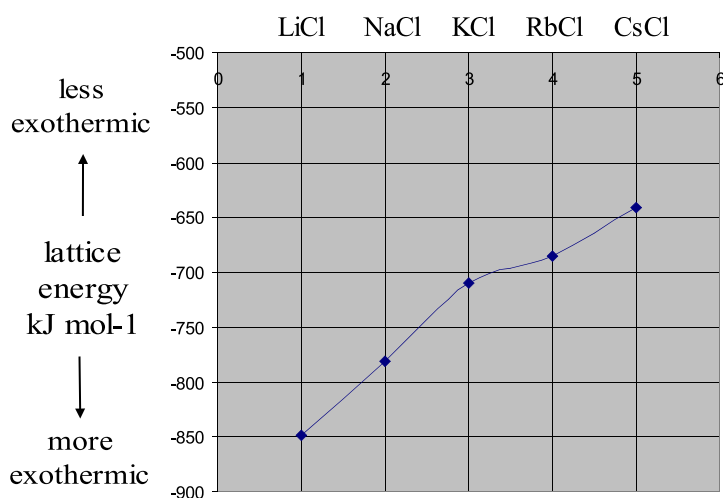
$$\Delta H_{\text{lattice energy}}^{\ominus} \propto \frac{(z_{\text{c}} \times z_{\text{a}})}{(r_{\text{c}} + r_{\text{a}})}$$

$z$  = the charge on the ion (**c**ation and **a**nion)

$r$  = ionic radius (of **c**ation and **a**nion)

The smaller the ions and the higher their charges (ie, the larger the *charge density*) the stronger the crystal lattice.

### Lattice energies of the alkali metal chlorides



Lattice energies decrease down the group corresponding with an increase in cation size.

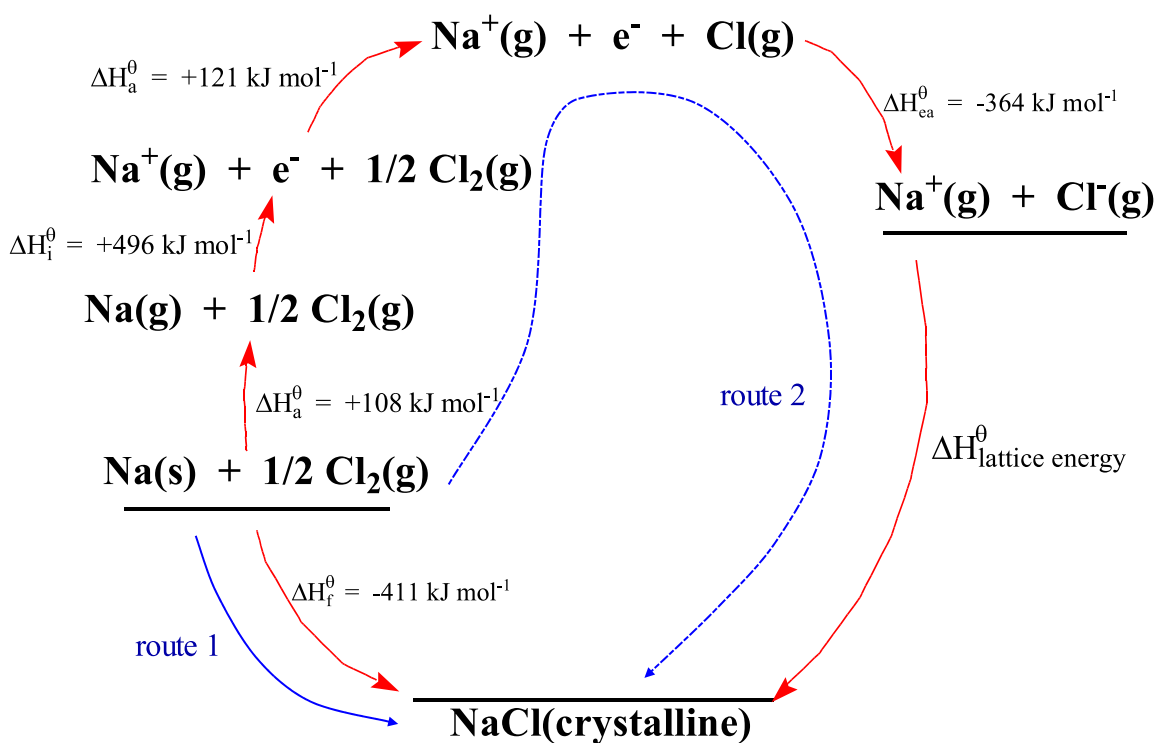


## Calculating lattice energies using the Born-Haber cycle

**Max Born (1882-1970)- Fritz Haber (1868-1934)**

The Born-Haber cycle is a routine, using readily available thermochemical data, for calculating *lattice enthalpies*.

eg,



**KEY:**

$\Delta H$  = enthalpy change  
a = atomisation  
i = 1st ionisation energy  
f = formation  
ea = 1st electron affinity

**Standard enthalpy of atomisation:**

The enthalpy change when 1 mole of gaseous, isolated, atoms of the element is formed from the element in its standard state.

Find the value of the lattice energy by applying Hess's law and equating routes 1 & 2: .....

## Chemical Energetics

route 1 = route 2

$$\Delta H_{f, \text{NaCl}}^{\theta} = -411 \text{ kJ mol}^{-1} = 108 + 496 + 121 + (-364) + \Delta H_{le}^{\theta}$$

$$\Delta H_{le}^{\theta} = -772 \text{ kJ mol}^{-1}$$

ie, when 1 mole of crystalline sodium chloride is formed from its isolated ions, 772 kJ of heat energy is liberated (or, it would require 772 kJ to completely separate the ions in 1 mole of crystalline sodium chloride)

Theoretical lattice enthalpies can be calculated using a formula which assumes **pure ionic** bonding in the metal compound.

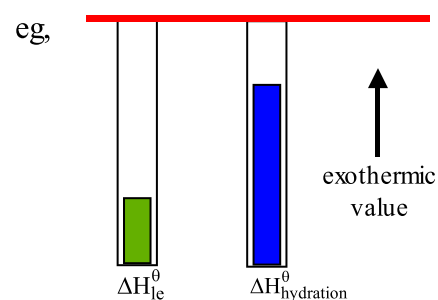
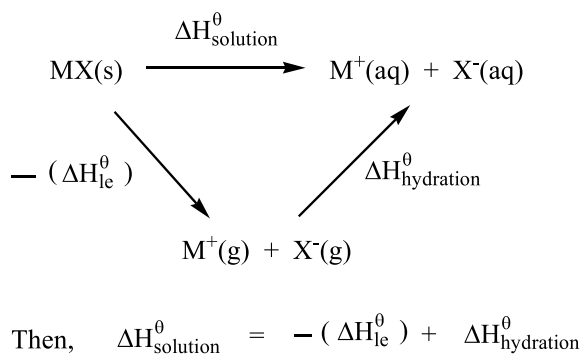
The greater the difference between this *calculated* lattice enthalpy value and the *experimental* value (using the Born-Haber cycle) the greater the electron sharing (covalency) between the ions.

The table below provides some examples.

compound	formula	Experimental (Born-Haber) lattice enthalpy kJ mol <sup>-1</sup>	Theoretical lattice enthalpy kJ mol <sup>-1</sup>	Degree of ionic character
Sodium chloride	NaCl	-772	-764	high
Potassium chloride	KCl	-680	-686	high
Cadmium iodide	CdI <sub>2</sub>	-2410	-1966	Medium, ....some covalency
Silver bromide	AgBr	-877	-759	Medium, ....some covalency

The more exothermic the lattice enthalpy the higher the *melting point* of the compound.

As a general rule the higher the lattice enthalpy the lower the *solubility* of the compound in water. However, solubility also depends on the total hydration enthalpy of the ions. If this is a high exothermic value it will counter the lattice enthalpy and enhance solubility.







In this case,  
compound readily soluble in water

## Chemical Energetics

In your exams you may be asked to discuss the solubilities of the group 2 hydroxides and sulphates in relation to trends in lattice enthalpy and hydration enthalpy down the group. The solubilities of these compounds were referred to in the *inorganic chemistry* theme.

The table below shows how the solubilities of these compounds compare.

Metal ion	Solubilities of the hydroxides (g/100 g water)	Enthalpy of solution of the hydroxides (kJ mol <sup>-1</sup> )	Solubilities of the sulphates (g/100 g water)	Enthalpy of solution of the sulphates (kJ mol <sup>-1</sup> )
Mg <sup>2+</sup> 	0.001	+2.8	33	-91.2
Ca <sup>2+</sup> 	0.16	-16.2	0.21	-17.8
Sr <sup>2+</sup> 	0.82	-46.0	0.013	-8.7
Ba <sup>2+</sup> 	4	-51.8	0.0002	+19.4

Increase in ion size  
down the group

**Increase** in solubility  
down the group

Increase in enthalpy  
of solution down the  
group

**Decrease** in solubility  
down the group

Decrease in  
enthalpy of solution  
down the group

As the group is descended the lattice enthalpies of the hydroxides and sulphates **decrease** as a result of an increase in metal ion size. For the same reason, the *total* hydration enthalpies of the ions of these compounds also **decrease** down the group.

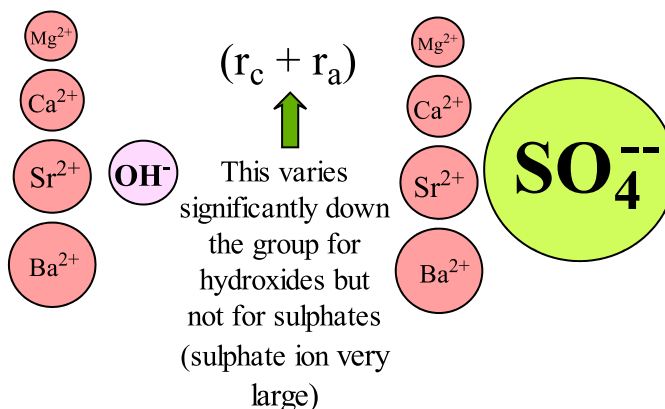
However, the **relative** decrease in *lattice enthalpies* and *total hydration enthalpies*, down the group, is not the same for both hydroxides and sulphates. For the hydroxides the decrease in lattice enthalpies dominates over the decrease in hydration enthalpies. For the sulphates its the other way about!

Hence the difference in solubility trends.

Remember:

$$\Delta H_{\text{lattice energy}}^{\oplus} \propto \frac{(z_c \times z_a)}{(r_c + r_a)}$$

$z$  = the charge on the ion (cation and anion)  
 $r$  = ionic radius (of cation and anion)



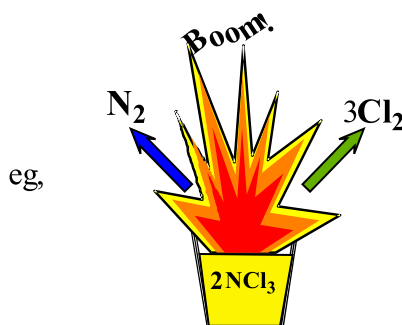
## Chemical Thermodynamics

This term simply means heat flow in chemical systems (the word *thermodynamics* derives from Greek words meaning *heat movement*).

The American physicist, **Josiah Willard Gibbs** (1839-1903), along with a number of other eminent chemists and physicists of that era, originated the ideas of modern chemical thermodynamics.

Most chemical reactions occur with evolution of heat; they are exothermic.

Some reactions are extremely vigorous and occur with explosive violence.

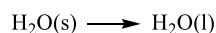
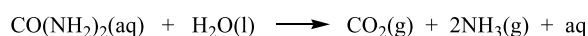
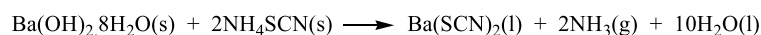
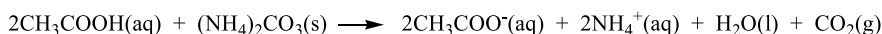
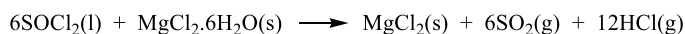


nitrogen trichloride is an unstable liquid. Traces of hydrocarbons or sunlight cause it to explode!



$$\Delta H_{\text{decomposition}}^{\theta} = -231 \text{ kJ mol}^{-1}$$

For this reaction the equilibrium constant  $K_p$  is very large and the enthalpy of decomposition is highly exothermic. Many other chemical reactions which have large equilibrium constants are also exothermic. As a result there is a temptation to equate reaction *feasibility* entirely with exothermicity. The more exothermic the more feasible! The problem with this is that there are some chemical processes which do **not** support this generalisation. The following, for example, are **endothermic** processes but occur readily with very little encouragement (occur spontaneously)!



Clearly, there is something about these reactions which, in spite of being endothermic, causes them to occur readily in the left to right direction. Looking at the equations we see that in six out of the seven cases the number of moles increases (moles of products exceed moles of reactants). In the seventh case (the last example) the water molecules become *disordered* as solid converts to liquid. We could say that in **all** cases molecular disorder increases! The reason why this disorder is helpful, in terms of reaction feasibility, is that a reacting system becomes more stable the greater the number of ways of arranging its molecules and sharing out their available energy. The term **entropy** (from the Greek meaning, *change*) is used to refer to molecular disorder. The symbol,  $S$  denotes entropy and  $\Delta S^{\theta}$  denotes standard entropy change. It has the units,  $\text{JK}^{-1}\text{mol}^{-1}$ . In spontaneous endothermic reactions, like those above, overall (total) entropy change is always positive (ie, increases, & markedly).

## Chemical Energetics

Lets cut to the chase!

You will need to remember these equations:

$$\Delta S_{\text{total}}^{\ominus} = \Delta S_{\text{reacting system}}^{\ominus} + \Delta S_{\text{surroundings}}^{\ominus}$$

$$\Delta S_{\text{reacting system}}^{\ominus} = S_{\text{products}}^{\ominus} - S_{\text{reactants}}^{\ominus}$$

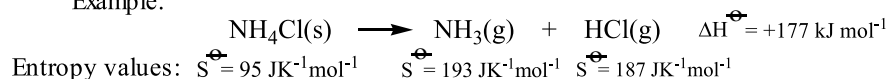
$$\Delta S_{\text{surroundings}}^{\ominus} = -\frac{\Delta H^{\ominus}}{T}$$

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T \cdot \Delta S_{\text{reaction}}^{\ominus}$$

$\Delta G^{\ominus}$  is known as the Gibbs function or, more commonly, free energy change

This is important because its the true indication of reaction feasibility. For a reaction to be feasible  $\Delta G^{\ominus}$  must be less than zero (ie, a negative value).

Example:



$$\Delta S_{\text{reacting system}}^{\ominus} = [(193 + 187) - 95] \text{ JK}^{-1}\text{mol}^{-1} = 285 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta S_{\text{surroundings}}^{\ominus} = -\frac{\Delta H^{\ominus}}{T} = -\frac{177 \times 10^3}{298} = -0.594 \times 10^3 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta S_{\text{total}}^{\ominus} = 285 + (-0.594 \times 10^3 \text{ JK}^{-1}\text{mol}^{-1}) = -309 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta G^{\ominus} = 177000 - 298 \cdot (285) \text{ JK}^{-1}\text{mol}^{-1} = 92 \text{ kJmol}^{-1}$$

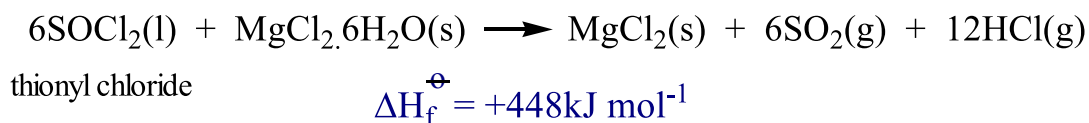
This large positive free energy change shows that the decomposition of ammonium chloride does not occur of its own accord at 298 K & 1 atm.

Overall entropy *decrease*. The entropy increase of the reacting system is swamped by the decrease in entropy of the surroundings. This indicates that ammonium chloride shows no inclination to decompose at 298 K.

In contrast, the reaction of ammonia with hydrogen chloride to give ammonium chloride (the reverse of the above reaction) has a  $\Delta S_{\text{total}}^{\ominus}$  of  $+309 \text{ JK}^{-1}\text{mol}^{-1}$  and a  $\Delta G^{\ominus}$  of  $-92 \text{ kJmol}^{-1}$  indicating a spontaneous reaction.

**(Note: *spontaneous reaction* - a reaction which occurs naturally, a reaction which is *feasible* for which free energy change is negative and total entropy change is positive.)**

## Chemical Energetics



**This is a highly *endothermic* reaction but one which occurs readily & with some violence at room temperature!**

On reaction, there is a large increase in volume corresponding with this large *increase* in entropy.

$$\Delta S_{\text{reaction}}^\ominus = 2560 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta G^\ominus = \Delta H^\ominus - T \cdot \Delta S_{\text{reaction}}^\ominus = [448000 - (298 \cdot 2560)] \text{ J mol}^{-1} = -315 \text{ kJ mol}^{-1}$$

A large, negative, Gibbs free energy change indicating a feasible and spontaneous reaction at room temperature and pressure.

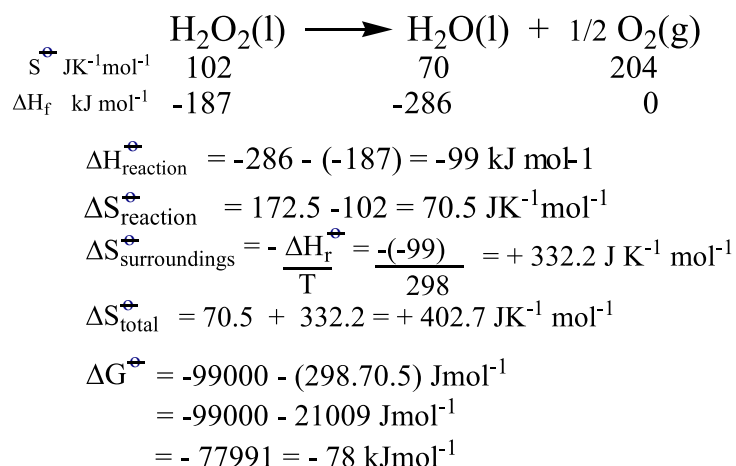
The reaction of hydrated barium hydroxide with solid ammonium thiocyanate is another strongly *endothermic* reaction which goes readily at room temperature and pressure.



It is a reaction which is sometimes demonstrated by the teacher. Suitable amounts of the reactants are placed in a conical flask. They are mixed, and the flask allowed to stand, for some minutes, on a wet piece of wood in the fume cupboard. After a while the wood becomes stuck to the flask due to the formation of ice between the surface of the wood and the bottom of the flask!

The reaction occurs readily because there is a large, overall, increase in entropy.

Hydrogen peroxide is a colourless liquid resembling water. It has a higher boiling point and a higher density than water. It will decompose into water and oxygen. How readily does this occur? We can get a good idea by calculating the entropy and free energy changes.



These results indicate what is born out in practice, namely, that hydrogen peroxide is an unstable substance readily converting to water and oxygen. The decomposition is catalysed by a variety of substances including powdered charcoal & transition metals & their ions. The decomposition of concentrated hydrogen peroxide solutions can occur explosively. Hydrogen peroxide is used in some rocket fuels since it is a convenient source of oxygen.



## Chemical Energetics

One final consideration.

If you find that, for a particular reaction, the total entropy change is *positive* and the free energy change is *negative* then you are dealing with a reaction which is feasible under the stated conditions. However, it may be that the reaction is still not spontaneous (does not occur automatically), under those conditions, because the *activation energy* is too high! We say that the reaction is *kinetically controlled*. The activation energy is the minimum energy the reactant molecules must have, when they collide with one another in the reaction mixture, in order for the reaction to get underway. Once the reaction is initiated it should proceed as thermodynamically predicted.

Activation energy is dealt with in the **chemical kinetics** theme.

# Theme Nine

The German chemist F.W. Ostwald & the Swedish chemist S.A. Arrhenius did much of the ground work developing the ideas & principles of reaction kinetics (1889).

## Chemical Kinetics

**This is concerned with the speed (or rate) of chemical reactions.**

Chemical reactions **do not** occur instantaneously.  
Some do occur very quickly but others are very slow.  
For example, the reaction of silver ions with chloride ions, in aqueous solution at room temperature and pressure, occurs rapidly. The white precipitate of silver chloride appears as soon as solutions of the ions are mixed.  
On the other hand, the oxidation of ethanol with acidified dichromate occurs more leisurely and the mixture requires heating in hot water to speed it up!

Rate of reaction can be defined as,  
*the amount of reactant which undergoes reaction in unit time (eg, per second or per minute) or the amount of product formed in unit time.*

Units:  $\text{mol dm}^{-3} \text{ time}^{-1}$

**Factors affecting the rate of chemical reactions:**

- **Temperature**
- **Concentration**
- **Physical state**
- **Catalyst**

### Temperature:

Increase temperature - increase rate.

Very roughly, --  $10^{\circ}\text{C}$  rise -- *doubles* the rate of reaction (don't take this too literally!).

**Collision theory** helps explain the effect of temperature:

Main points of the collision theory:

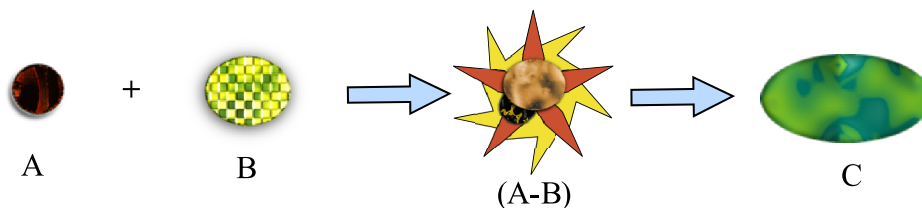
- Molecules *must collide* in order to react.
- Molecules must collide *in the correct orientation* to react.
- Molecules must have the *optimum amount of energy* (known as the **activation energy**) to react.

**Activation energy** can be defined as: *the minimum amount of energy colliding molecules must have in order to react (--when bonds break and new bonds form).*

Raising the temperature increases the *kinetic energy* of the reacting molecules.

This means that their *translational, rotational and vibrational* energies increase and as a result, they will collide more frequently and are more likely to have the required activation energy.

## Chemical Kinetics



The structure labelled (A-B) represents the **transition state**. It is formed when the reactant molecules have the required **activation energy**.

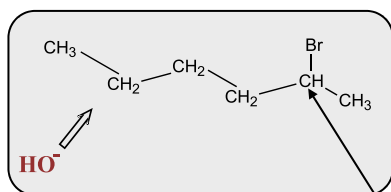
If two reactant molecules collide with sufficient activation energy they can combine to form products. If, on collision, they do not have the required activation energy they will simply bounce apart and not react.

Importance of correct  
ORIENTATION of reacting  
molecules:

eg,

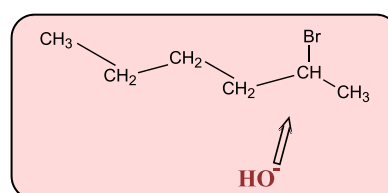
2-bromohexane is hydrolysed in warm alkali to hexan-2-ol. However, in order for reaction to be effective the hydroxide ion must collide with the carbon atom to which the bromine is attached. Clearly, unless the molecules are orientated correctly, product formation will not occur even when the colliding molecules have energy in excess of the activation energy.

Incorrect orientation.



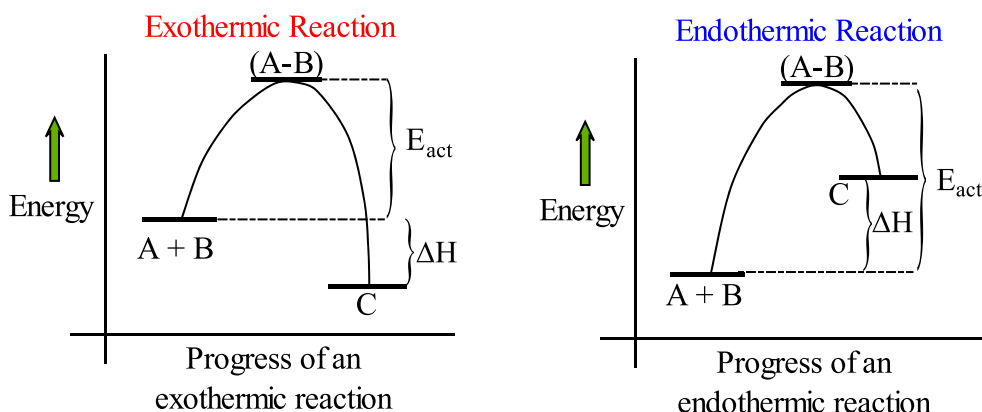
required reaction site

Correct orientation



## Chemical Kinetics

Reaction profiles are energy level diagrams showing the relationships between reactants, transition state and products.

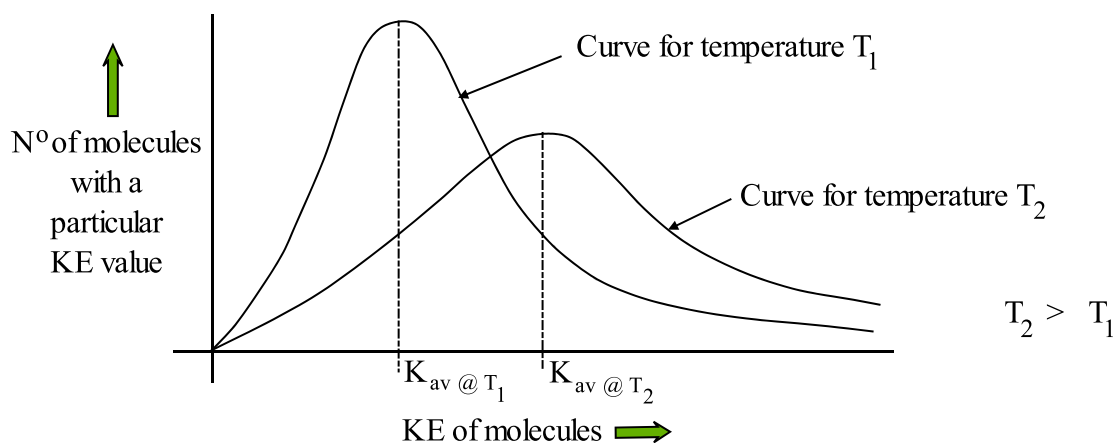


Maxwell-Boltzmann energy distribution curves provide another way of showing the effect of temperature on the kinetic energy of molecules and rate of reaction.

(James Maxwell - Scottish mathematician and physicist 1831 - 1879

Ludwig Boltzmann - Austrian physicist 1844 - 1906)

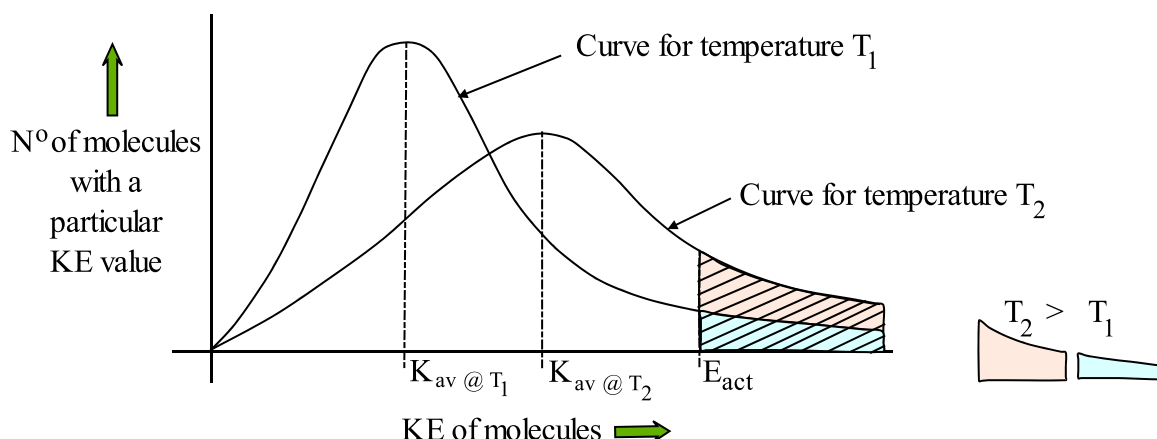
These scientists emphasised that at a particular temperature a group of molecules such as those in a reaction mixture, will have a range of energies. Some molecules having energies greater than the average and some having energies less than the average. The graphical representation of this is known as a Maxwell-Boltzmann distribution curve.



## Chemical Kinetics

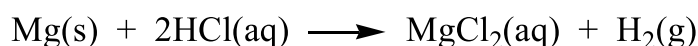
At the higher temperature more molecules are likely to have the reaction activation energy ( $E_{\text{act}}$ ) and undergo reaction on collision..

The coloured areas, underneath the curves, are proportional to the number of molecules having energies greater than  $E_{\text{act}}$  .



## Concentration:

To see how concentration affects rates of reactions let's have a look at the reaction of magnesium with hydrochloric acid.



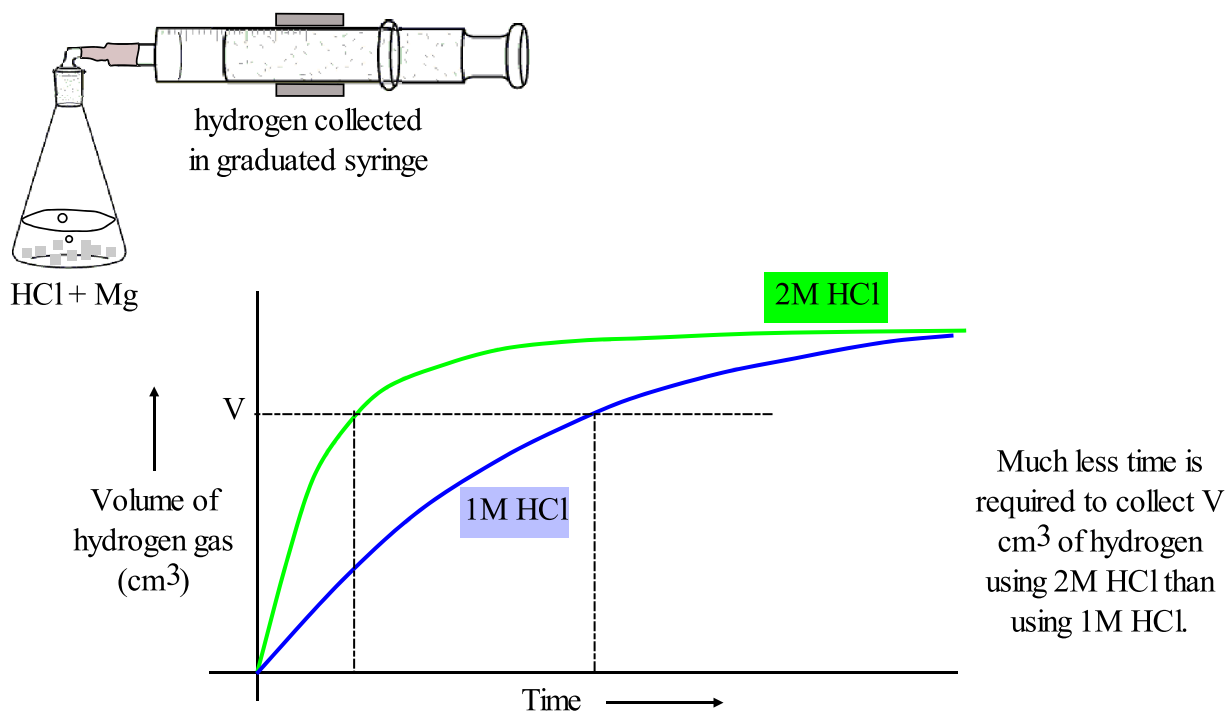
Experiments show that the more concentrated the acid the more quickly the magnesium is used up. This is no great surprise because increasing the concentration of the acid increases the frequency of collision between hydrogen ions and the metal so increasing the chance of reaction.

This is a general result. ***Increasing the concentration of reactants increases the rate of reaction.***

The relationship between rate and concentration is sometimes straight forward, such as simple direct proportionality, but on other occasions the relationship is more complex. For this Mg/HCl reaction, for example, experiment shows that rate is proportional to the acid concentration squared. This means that when the acid concentration is doubled the rate quadruples!

## Chemical Kinetics

The rate of the Mg/HCl reaction can be monitored by measuring how quickly hydrogen is evolved.

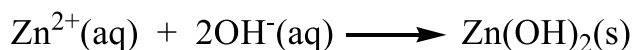


## Physical State of Reactants

The more finely divided the reactants the more readily the reaction takes place.

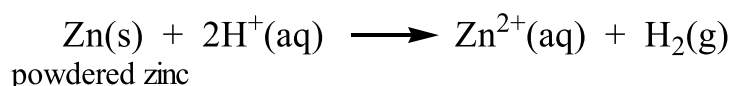
General order of reactivity, *in terms of physical state*: gaseous reactants > liquid reactants > solid reactants.

eg,



Reactants in the aqueous phase

The white precipitate of zinc hydroxide is formed quickly.



One of the reactants in the solid phase

The zinc reacts in a leisurely fashion; not a particularly rapid reaction!

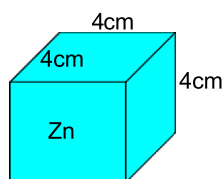
The reaction is very slow if *granulated* zinc is used rather than powdered zinc.

## Chemical Kinetics

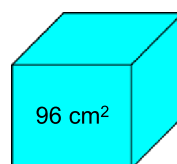
By using finely divided reactant the number of atomic or molecular collisions is increased and the rate of reaction increases.

You may be able to appreciate the importance of particle size and surface area, a little better, by considering the following:

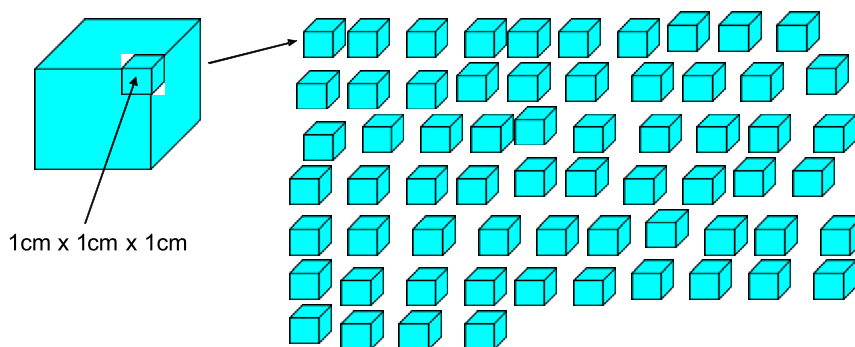
**Imagine a cube of zinc.**



This has a **surface area** of  $96 \text{ cm}^2$ .



It can be broken down into 64 small cubes each of these having a surface area of  $6 \text{ cm}^2$



Total surface area of the small cubes =  $64 \times 6 \text{ cm}^2 = 384 \text{ cm}^2$

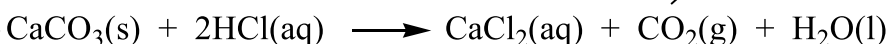
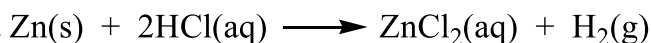
ie,  $384/96 = 4$  times larger surface area

ie, A given mass of material presents a larger surface area the more finely divided it is.

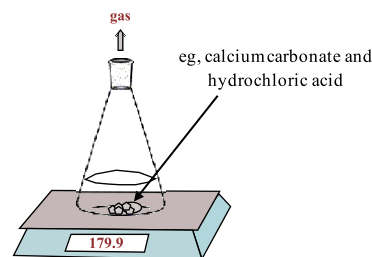
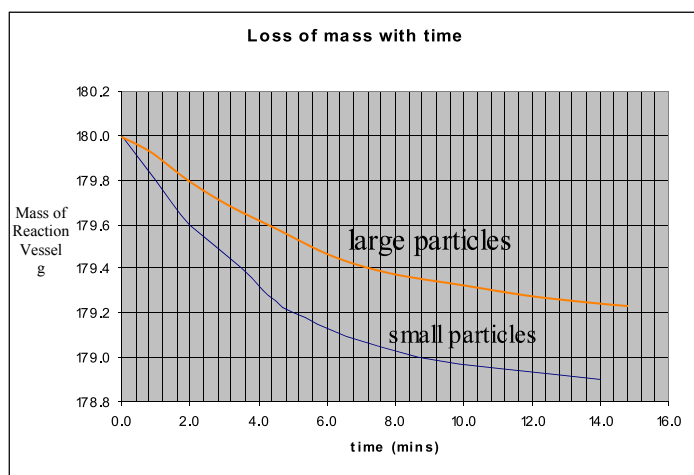
## Investigate particle size

We can demonstrate the effect of particles size on rate of reaction by carrying out a reaction which involves solid reactant and gives a gaseous product. As the reaction proceeds and gas is lost to the atmosphere, the overall mass of the reaction mixture *decreases*. This can be measured and recorded and shown to depend on the particle size of the solid reactant.

eg, we can investigate reactions such as:



Change the size of the particles of these reactants and see what effect a given mass of the reactant has on the rate of evolution of gas.



## Catalyst

*A catalyst is a substance which speeds up a chemical reaction by providing an alternative, less energetic, route to products without itself being used up.*

The word *catalyst* derives from the Greek meaning, *dissolves*.

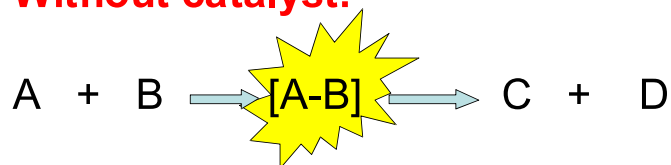
**Jons Berzelius** (1835) was the first to use the term in relation to rates of chemical reactions.



## Chemical Kinetics

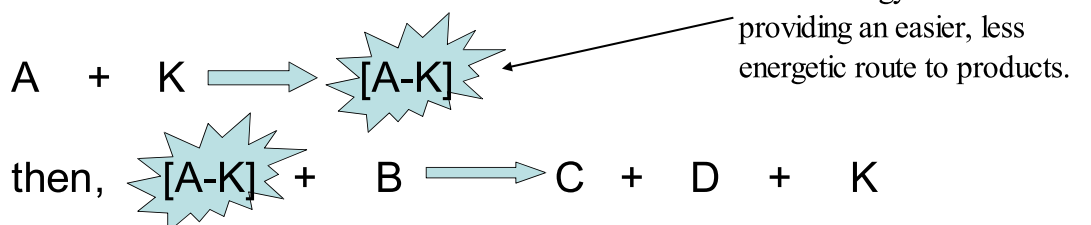
In general terms:

**Without catalyst:**

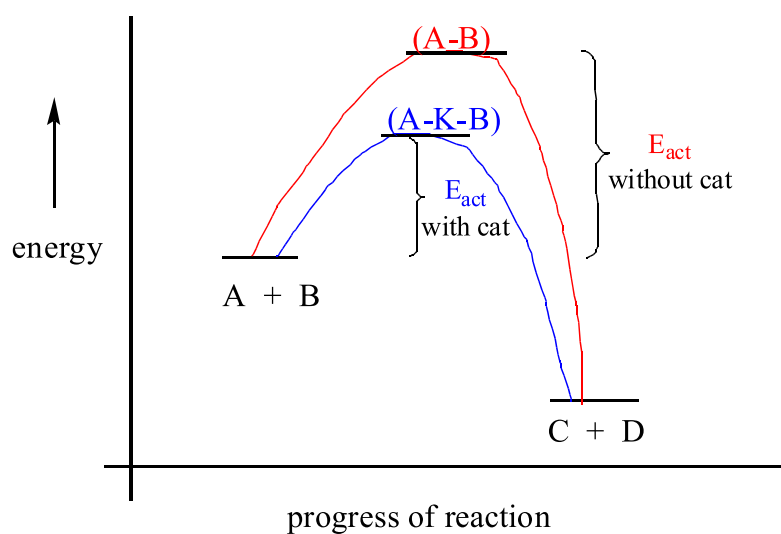


This is the normal, high energy, requirement.

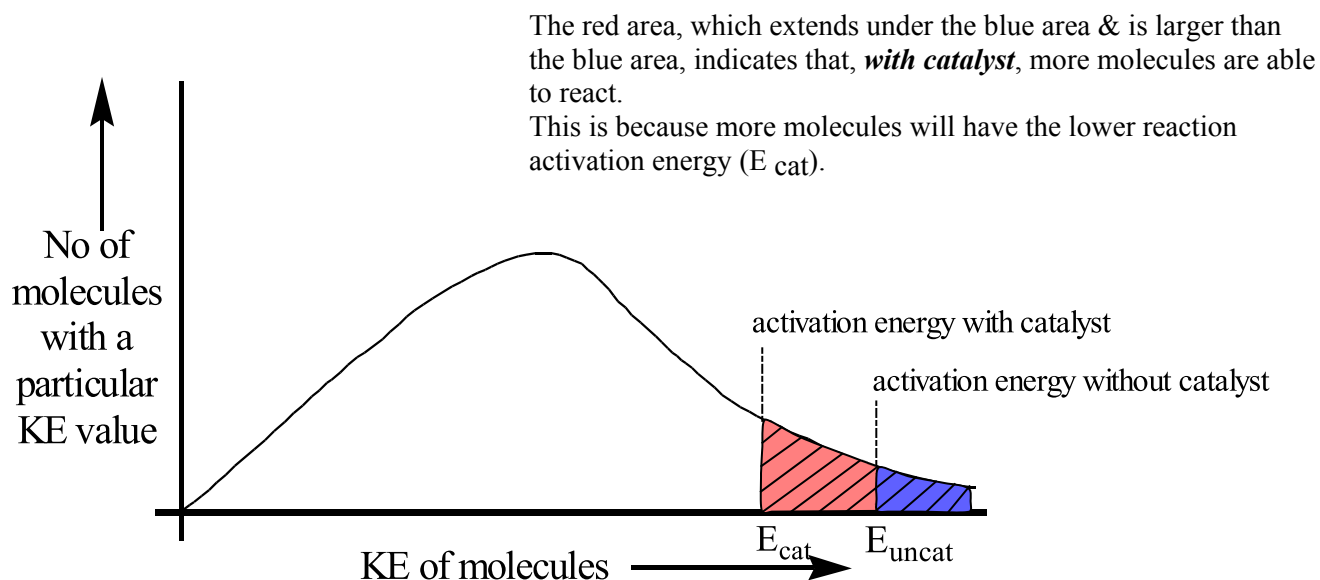
**With catalyst (K):**



Reaction profiles are helpful in showing how a catalyst alters the energetics of reaction:



## Distribution curve

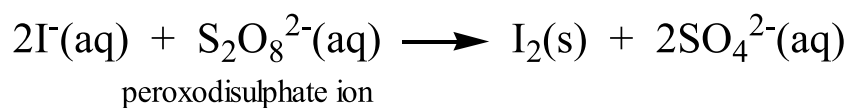


## Types of catalyst:

### 1. Homogeneous catalysts

Catalyst in *same* physical state as the reactants.

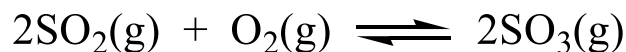
eg,  $\text{Fe}^{2+}(\text{aq})$  catalyses the following reaction:



### 2. Heterogeneous catalysts

Catalyst in *different* physical state to the reactants.

eg,  $\text{V}_2\text{O}_5(\text{s})$  catalyses the reaction between sulphur dioxide and oxygen to give sulphur trioxide:

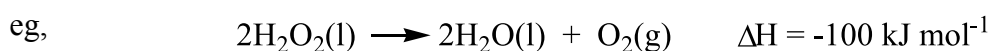


## Thermodynamic & Kinetic Stability

Generally, reactions which are overall exothermic stand a better chance of success!

This is because there is a natural tendency for high energy reactants to convert into more stable, low energy, products.

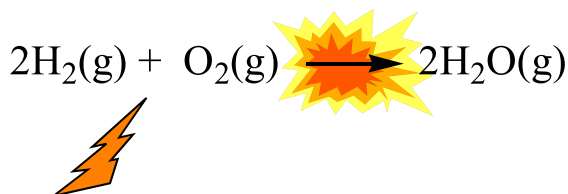
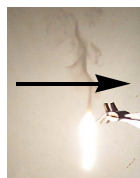
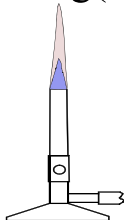
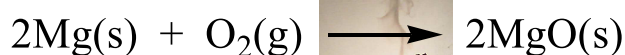
The reactants are said to be thermodynamically unstable with respect to products.



The hydrogen peroxide is **thermodynamically unstable** with respect to the water.

Although many reactions are exothermic they do not occur *spontaneously*, they require application of energy to get them started.

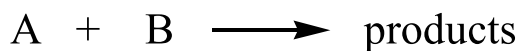
eg,



In these cases the reactions have high activation energies and do not occur unless this minimum amount of energy is available. The reactants are said to be **kinetically stable**.

## Rate equation & Order of reaction

For,



Experiment shows:

$$\text{rate} = k [A]^x [B]^y$$

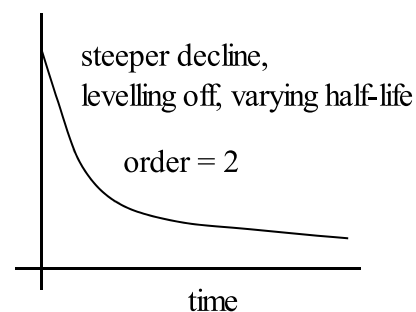
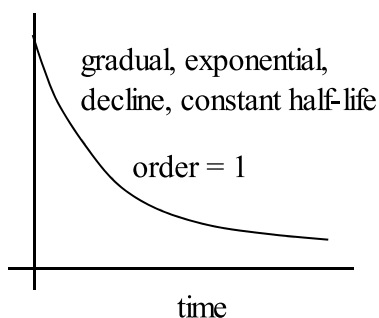
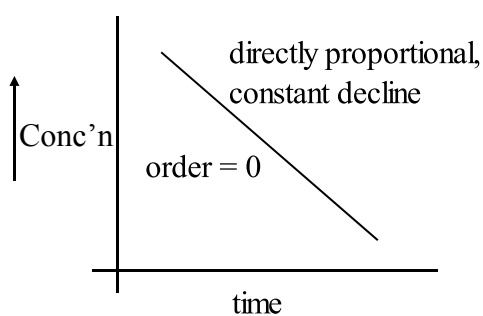
rate constant

rate equation

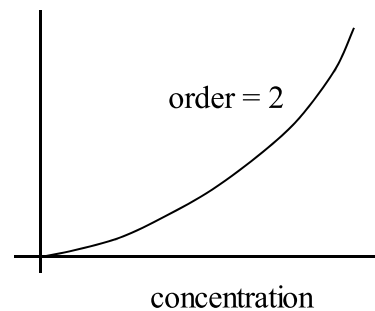
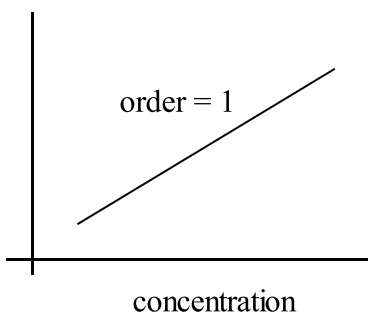
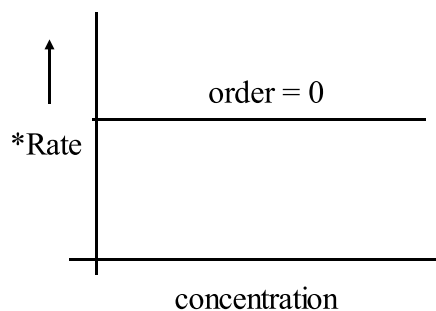
These powers often have the values 0, 1, 2, or 3 they are called **orders**.  
The overall order (or, **reaction order**) = (x+y).

## Determination of Order of Reaction

1. Perform a series of experiments measuring the variation of concentration of a reactant with time. Plot the results. The shape of the line indicates the order with respect to the reactant whose concentration is varying.



Alternatively, plot rate against concentration. Again the shape of the lines indicate the order with respect to the reactant.



\*(rates obtained by taking tangents to the curves on the concentration/time graphs)

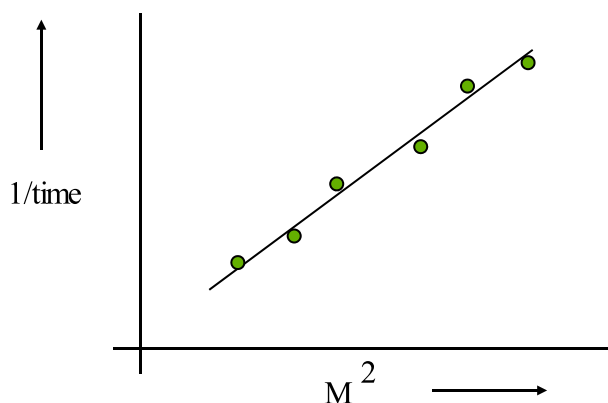
## Chemical Kinetics

2. Plot a series of graphs of rate of reaction against concentration raised to various powers. Decide which power value provides a straight line relationship.

eg,

Take a small length (eg, 2 cm) of clean magnesium ribbon and drop it into an excess of 1M hydrochloric acid. Record how long it takes to dissolve. Repeat the experiment using different molarities of dilute acid. In each case record how long it takes for the 2 cm length of magnesium ribbon to dissolve.

Plot reciprocal time (proportional to rate) against concentration squared.



Therefore,

$$\text{Rate} = k (\text{concentration})^2$$

The reaction of magnesium with hydrochloric acid is second order with respect to the acid.

3. Inspecting simple rate data.

eg,

Two reactive gases (arbitrarily represented P & Q) combine readily to give compound  $PQ_2$ . Experiments are performed to discover, (i) the effect, on rate, of changing the concentration of Q, (ii) the effect, on rate, of changing the concentration of P. Temperature being maintained constant throughout.

Experiment	Initial [P] $\text{mol dm}^{-3}$	Initial [Q] $\text{mol dm}^{-3}$	Initial rate of formation of product $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.10	0.10	0.001
2	0.10	0.20	0.004
3	0.10	0.30	0.009
4	0.20	0.10	0.001
5	0.30	0.10	0.001

From experiments 1 & 2, rate  $\propto [Q]^2$  since doubling  $[Q]$  quadruples the rate.  
Rate is *second order* with respect to Q.

From experiments 1 & 4, rate  $\propto [P]^0$  since doubling  $[P]$  does not alter the rate.  
Rate is *zero order* with respect to P.

The overall rate equation: rate =  $k [Q]^2$ , ie, the reaction is *overall second order*.

↙ This type of data presentation is popular in GCE chemistry exams!

4. Fit experimental data to *theoretical rate equations*.

It can be shown:

For a first order reaction,

$$t = \frac{2.303}{k} \log \left( \frac{a}{a-x} \right)$$

$t$  = time from start of experiment  
 $k$  = rate constant  
 $a$  = initial  $[A]$  of reactant A  
 $(a-x)$  = amount of A remaining at time  $t$

For a first order reaction, half-life =  $0.693/k$ , ie, it is constant & independent of the initial concentration ( $a$ ). You could plot a graph of concentration against time and see whether half-life is constant. It will be if its first order!

For a second order reaction,

$$t = \frac{1}{k} \cdot \frac{x}{a(a-x)}$$

this equation assumes that reactants A & B are present in equal amounts to begin with

The half-life of a second order reaction:  $t_{0.5} = \frac{1}{k \cdot a}$

ie, half-life depends on the initial concentration,  $a$

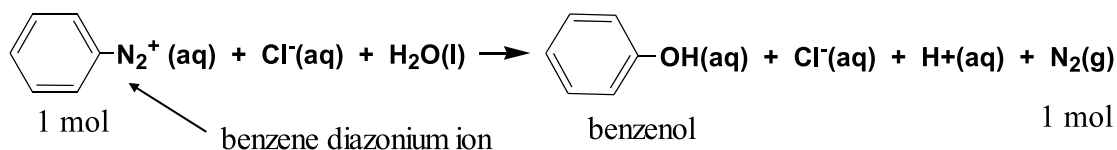
A graph of concentration against time gives a variable half-life for a second order reaction.

## Monitoring change in concentration of a reactant with time

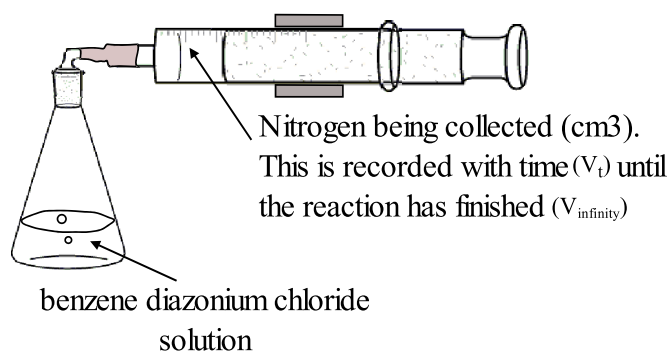
1. If the reactants are acids or bases they can be monitored by titration or by pH measurement.
2. If they are coloured it may be possible to monitor concentration change using a colorimeter.
3. If gas is evolved its volume can be measured with time and this related to the amounts of reactants at various times.

## Examples:

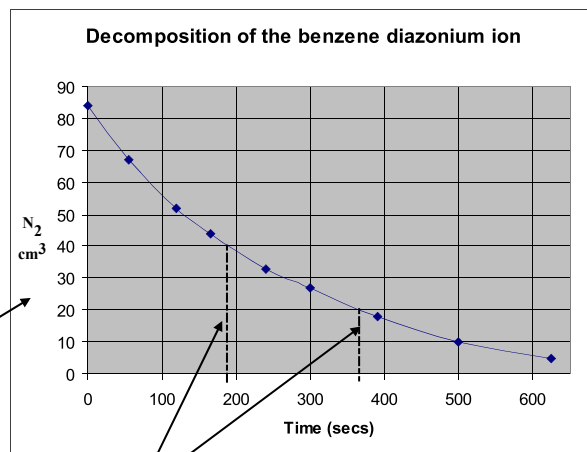
### Monitoring the decomposition of benzene diazonium chloride solution:



The rate of decomposition is related directly to the volume of nitrogen evolved.



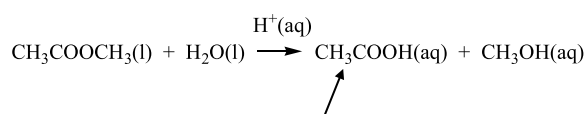
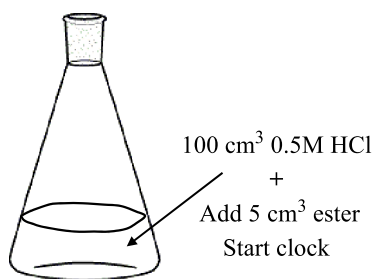
Volume of nitrogen remaining to be collected ( $V_{\infty} - V_t$ ). This is directly proportional to the amount of diazonium ion in solution



These half-life intervals are constant

These results indicate that the decomposition of the benzene diazonium ion is first order,  $\text{rate} = k [\text{diazonium ion}]$

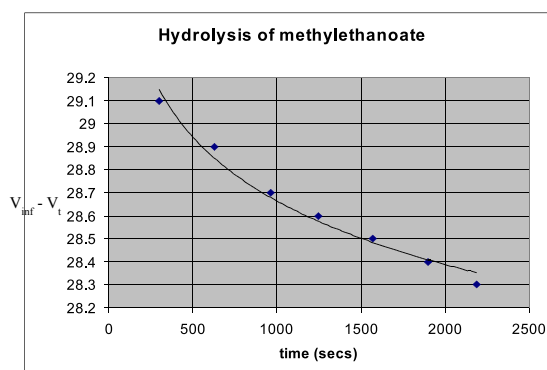
### Monitoring the acid catalysed hydrolysis of methyl ethanoate:



This, plus some HCl, is being titrated against the NaOH

Withdraw 5 cm<sup>3</sup> samples of the reaction mixture at regular intervals over 40 mins. Quench these in 100 cm<sup>3</sup> of iced water and titrate against standard NaOH solution ( $V_t$ ). Take a final sample after a week ( $V_{\infty}$ ). Maintain the reaction mixture at constant temperature throughout.

Amount of ester remaining at time,  $t$ , proportional to ( $V_{\infty} - V_t$ ). Plot results.



Results indicate first order with respect to ester.  $\text{Rate} = k[\text{ester}]$ . Could confirm by taking tangents, at various points on the curve, and plot rate against concentration to give a straight line relationship.

## Reaction Mechanism

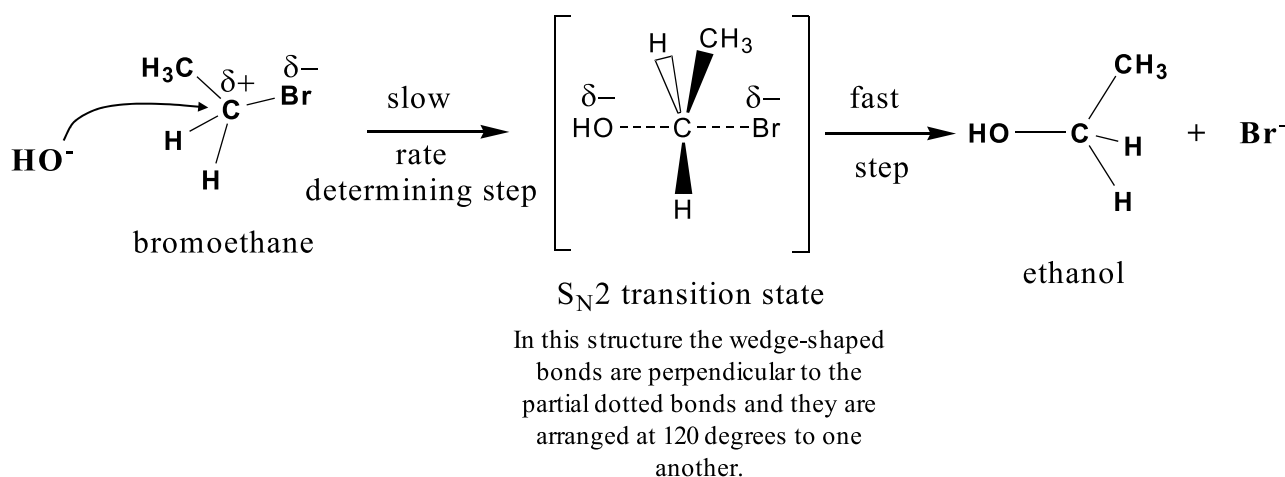
*A reaction mechanism is a series of steps showing in some detail how reactants are converted to products.*

eg, hydrolysis of bromoethane in sodium hydroxide solution

Experiments show that,  $\text{rate} = k[\text{C}_2\text{H}_5\text{Br}][\text{OH}^-]$  ie, *overall* second order.

This suggests that the mechanism involves a slow step in which hydroxide ion combines with bromoethane to give a transition state which then converts to products.

The kinetics support the following, accepted, mechanism:



## More activation energy!

We can define activation energy as, *the minimum amount of energy required to initiate the reaction and form transition states.*

The Swedish chemist, [Svente Arrhenius](#) (1889) was the first to show the relationship between the rate constant, for a reaction, and the temperature and activation energy. The relationship is known as the Arrhenius equation.

ie,

$$k = A \cdot e^{-E/RT}$$

$T$  = absolute temperature  
 $R$  = gas constant (8.31 J per degree K per mol)  
 $k$  = rate constant  
 $A$  = Arrhenius constant  
 $E$  = activation energy



## Chemical Kinetics

The Arrhenius equation provides a method of determining activation energy values by measuring the rate constant at various temperatures.

For this purpose it is convenient to re-write the equation in log to the base 10 form.

ie,

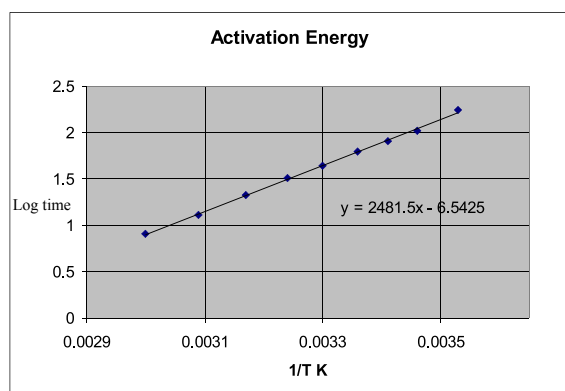
$$\log k = \log A - \frac{E}{2.303RT}$$

Since the time,  $t$ , taken for a given quantity of reactant to form, or reactant to be used up, is inversely proportional to the rate constant,  $k$ , then,

$$\log t = \frac{E}{2.303RT} + \text{constant}$$

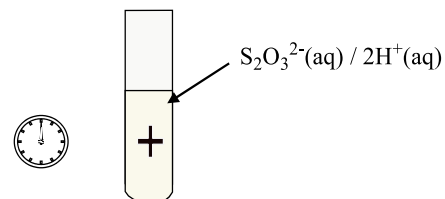
A plot of  $\log t$  against  $1/T$  K will give a straight line whose gradient is  $E/2.303R$ , hence a value for  $E$ .

eg. For the reaction:  $\text{S}_2\text{O}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{S}(\text{s})$



from the slope (2481.5),  
 $E = +47.5 \text{ kJ mol}^{-1}$

At a particular temperature, note how long it takes for colloidal sulphur to obscure a cross marked, using marker pen, on the far side of the reaction vessel. Repeat at other temperatures & plot results.



Refer to J.W.Turner, SSR 1972,53,751 for further detail.

# Theme Ten

## Organic Chemistry I

### Organic Chemistry

#### Introduction:

Definition:

*The discovery and investigation of natural and synthetic materials containing carbon.*

More than 6 million organic compounds are known. These range from the very simple to the very complex.

eg,

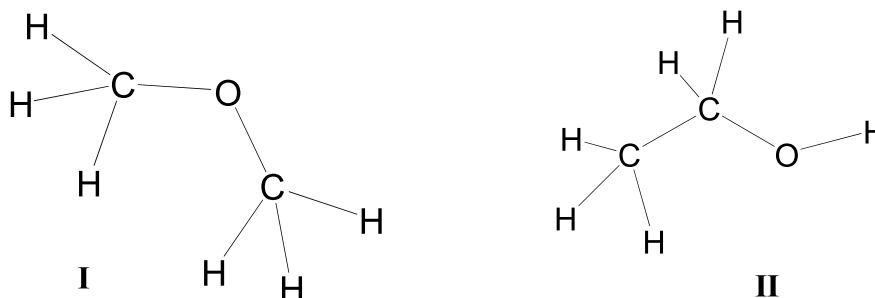
Name	Molecular Formula
methane	$\text{CH}_4$
ethane	$\text{C}_2\text{H}_6$
vitamin B <sub>12</sub>	$\text{C}_{65}\text{H}_{88}\text{N}_{14}\text{O}_{14}\text{PCo}$
$\alpha$ -chlorophyll	$\text{C}_{55}\text{H}_{75}\text{O}_6\text{N}_4\text{Mg}$

Organic compounds are classified according to their chemical properties.

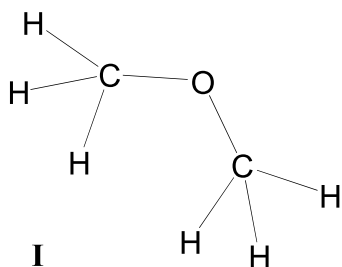
The chemical properties are determined by the type of atoms and the way in which they are arranged in the molecules.

eg,

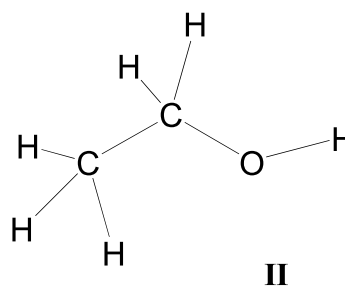
The following two compounds have the same number of atoms of the same elements but because the atoms are connected together differently they have different chemical properties.



## Organic Chemistry I



methoxymethane  
an ether  
An unreactive compound



ethanol  
an alcohol  
A reactive compound

Small groups of atoms, called **functional groups**, are largely responsible for the chemical properties of organic molecules.

Functional group	Structure of functional group	Name of functional group
<b>-CH<sub>2</sub>OH</b>		primary alcohol
<b>-CHO</b>		aldehyde
<b>&gt;CO</b>		ketone
<b>-COOH</b>		carboxyl (or carboxylic acid)
<b>-CH<sub>2</sub>NH<sub>2</sub></b>		primary amine

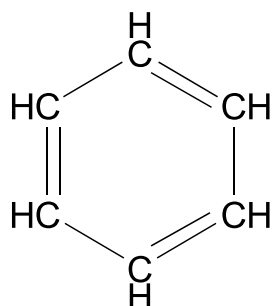
Compounds containing the same functional group are said to belong to the same **homologous series**.

Molecules in the same series have similar chemical properties.

Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) and propanol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ), for example, have similar chemical properties because they both have a *primary alcohol* group.

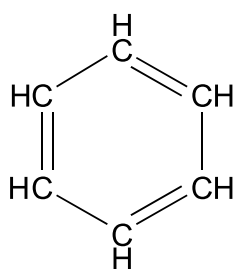
A further distinction is made between, **aliphatic** and **aromatic** compounds.

Aromatic compounds include all those containing the **benzene ring**.



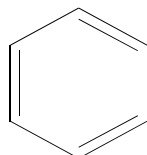
Benzene, itself, has the molecular formula,  **$\text{C}_6\text{H}_6$** .

Its characteristic structural feature is a ring of six carbon atoms held together by alternate single and double bonds.

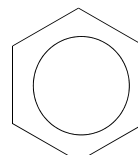


structural formula

}



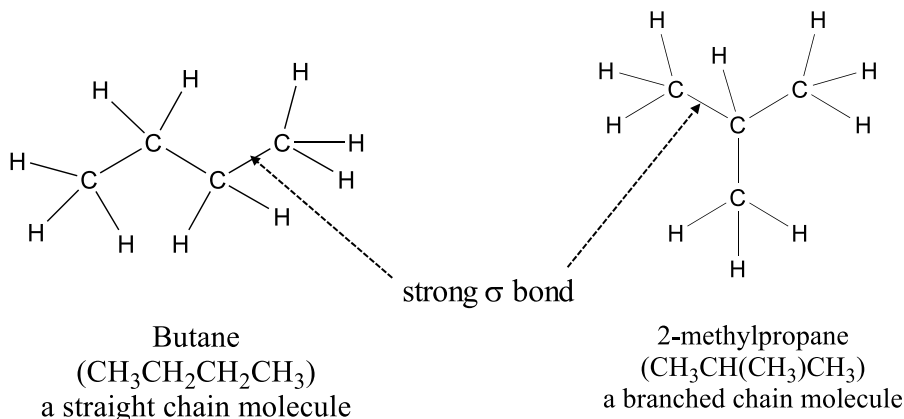
or



symbols

Aliphatic compounds are all those which do not contain a benzene ring and have **straight** or **branched** chain molecules.

Eg,

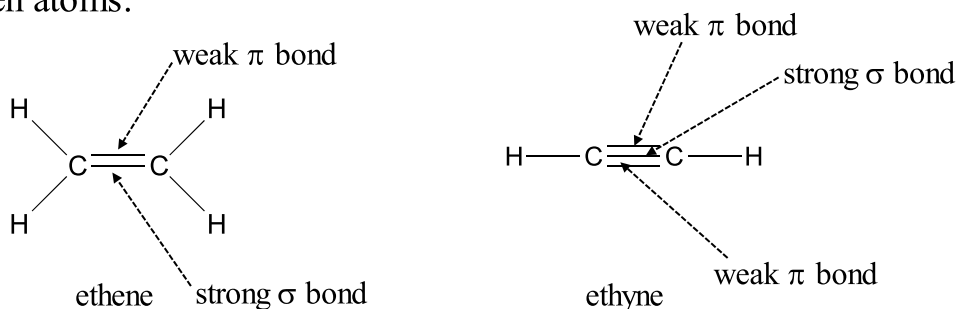


These aliphatic compounds are **saturated** hydrocarbons.

The term means that the bonds between the carbon atoms are single, strong, covalent bonds (sigma ( $\sigma$ ) bonds) and that the carbon atoms are attached to their full quota of hydrogen atoms.

If the carbon atoms are linked with double or triple carbon-carbon bonds they are said to be **unsaturated** because the carbon atoms are not attached to their full quota of hydrogen atoms.

eg,



**Unsaturated compounds are generally more reactive than saturated compounds because the pi bonds are relatively easy to break and therefore more reactive than the sigma bonds.**

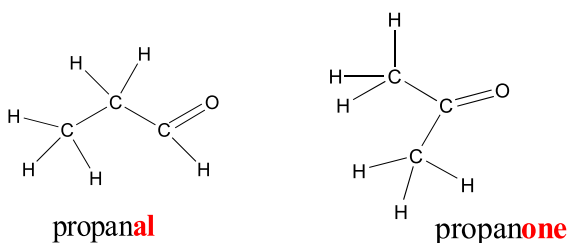
Referring to the ether (I) and alcohol (II) shown on page 85. They are examples of **structural isomers**.

They have the same molecular formula but different arrangements of atoms.

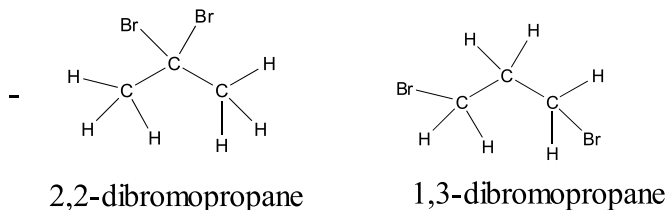
Because they have different functional groups they are examples of **functional group structural isomers**.

## Further examples:

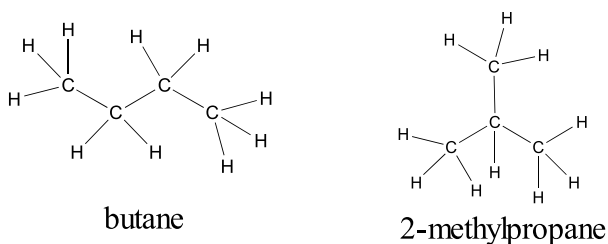
Functional group structural isomers -



Position structural isomers



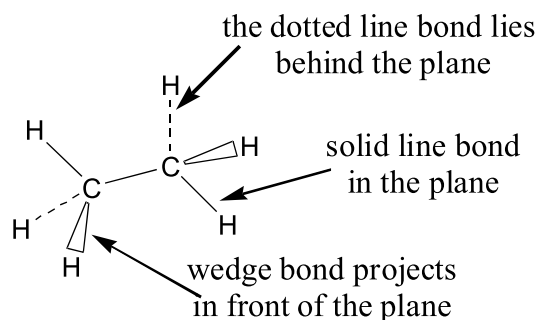
Chain structural isomers -



Molecules containing saturated carbon atoms have 3-dimensional structures, ie, they are **not** planar (not flat) molecules.

*Wedge* and *dotted* line bonds are often used to depict 3-dimensional structures.

eg,



The shape, or conformation, of this ethane molecule is particularly stable because the bonding pairs are situated as far away from one another as possible.

## Electrophiles and Nucleophiles.

These are terms used to refer to certain atoms or groups.

*An electrophile is an electron seeking atom or group which accepts a pair of electrons to form a covalent bond.*

Important electrophiles include, the hydrogen ion ( $\text{H}^+$ ), the nitronium ion ( $\text{NO}_2^+$ ) and the sulphur trioxide molecule ( $\text{SO}_3$ ). Electrophiles are examples of **Lewis acids** (they can accept an electron pair to form a covalent bond).

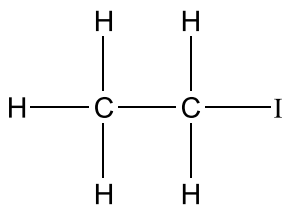
*A nucleophile is an atom or group which is electron rich and can provide a pair of electrons to form a covalent bond.*

Important examples include, the hydroxide ion ( $\text{OH}^-$ ), halide ions (eg,  $\text{Br}^-$ ) and the nitrile ion ( $\text{CN}^-$ ). Nucleophiles are examples of **Lewis bases** (they can provide an electron pair to form a covalent bond).

## Naming Organic compounds (organic nomenclature)

For the purpose of naming, organic compounds are considered as derivatives of hydrocarbons.

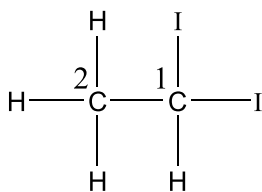
Eg,



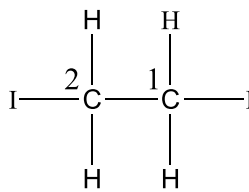
This is called **iodoethane**

It is a derivative of ethane in which a single hydrogen has been replaced by an iodine atom.

If **two** hydrogen atoms are replaced by iodine, two different compounds are possible.



1,1-diiodoethane



1,2-diiodoethane

The numbers indicate the carbon atoms to which the iodines are attached. The carbon atoms are numbered to give the *lowest* numbers in the name.

## The Alkanes

These hydrocarbons have the general formula,  $C_nH_{2n+2}$  where  $n$  is an integer 1, 2, 3, 4, etc. They form a homologous series.

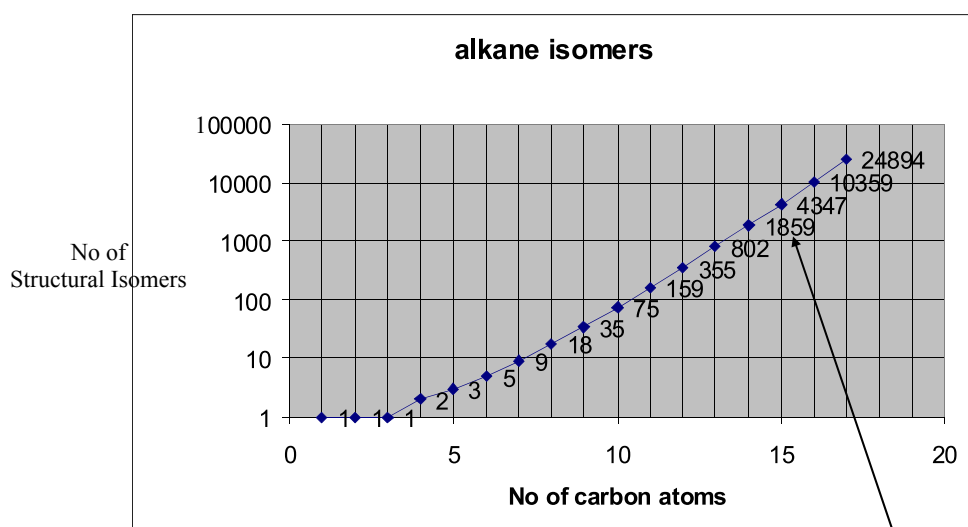
ie,

alkanes	formula	b.pt °C	structural isomers
methane	CH <sub>4</sub>	-162	1
ethane	C <sub>2</sub> H <sub>6</sub>	-89	1
propane	C <sub>3</sub> H <sub>8</sub>	-42	1
butane	C <sub>4</sub> H <sub>10</sub>	0	2
pentane	C <sub>5</sub> H <sub>12</sub>	36	3
hexane	C <sub>6</sub> H <sub>14</sub>	69	?
heptane	C <sub>7</sub> H <sub>16</sub>	98	9
octane	C <sub>8</sub> H <sub>18</sub>	126	18
eicosane	C <sub>20</sub> H <sub>42</sub>	220at 30 mm	366319

**-CH<sub>2</sub>-**  
is the *homologous increment*

It's the difference between successive members in the series

How many?  
(see below)



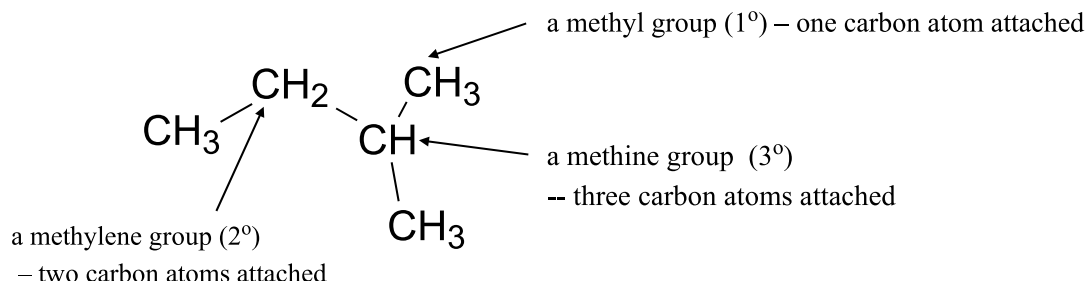
30 carbon atoms – 4 111 846 766 isomers !

number of isomers



Carbon atoms in molecules are sometimes referred to as, primary ( $1^\circ$ ), secondary ( $2^\circ$ ) or tertiary ( $3^\circ$ ).

eg,



## Chemical Properties of Alkanes:

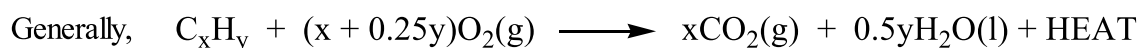
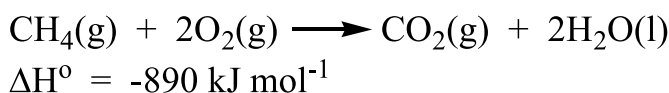
They are relatively unreactive.

They will, however, react with *oxygen* and with *halogens*.

### With oxygen

They burn readily in oxygen with a *clean* flame and producing a great deal of heat.

eg,

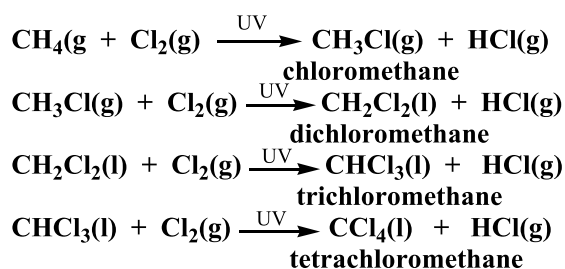


As a result of this reaction, alkanes are important as fuels.

### With halogen

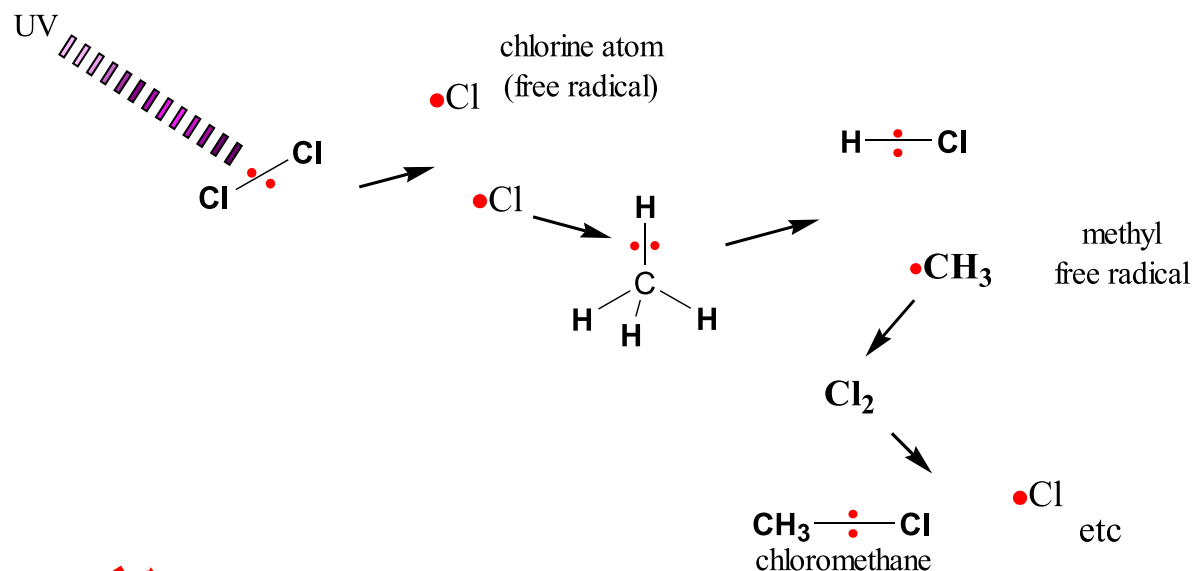
In the presence of ultra-violet light the alkanes react with the halogens forming **substitution** products known collectively as **halogenoalkanes** (or just *haloalkanes*). However, reactivity *decreases* down the halogen group. A number of substitution products are possible.

eg,



These reactions occur very readily because **free radicals** are involved

Free radicals have an unpaired electron. They are generally very reactive, readily getting involved in reactions in which they can share their unpaired electron with another atom. Free halogen atoms provide examples of **free radicals**.



## Fuels

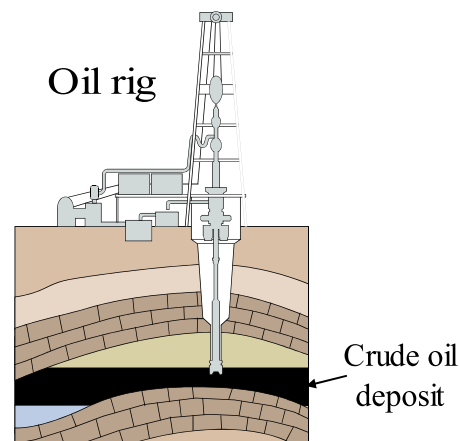
Most of our fuels are hydrocarbon based and non-renewable. They are derived from natural coal, oil and gas supplies.

The aim of industrial nations, like our own, is to develop **renewable** sources of energy employing sun, wind, tides, water (*as a source of hydrogen*) and plant material. In addition, research continues to make more efficient use of traditional energy sources (including nuclear power).

Characteristics of an **ideal** fuel:

- Easily obtained and an inexhaustible supply.
- Provides a very large amount of energy from a very small amount of fuel (high **calorific value**).  $\longrightarrow$
- Non-toxic and safe to handle and use.
- Non-toxic waste products.

**None of the fuels we use today are ideal in terms of these criteria.**



Calculating **calorific values** ( $\text{kJ g}^{-1}$  &  $\text{kJ cm}^{-3}$ ):  
eg,

Octane:  $\Delta H_c = 5512 \text{ kJ mol}^{-1}$

Molar mass of octane =  $114 \text{ g mol}^{-1}$

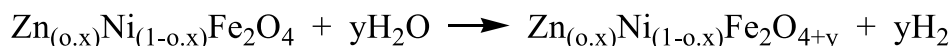
1g of octane provides,  $(1/114) \times 5512 \text{ kJ}$   
=  $48.4 \text{ kJ}$

The density of octane at rtp is  $0.7 \text{ g cm}^{-3}$

1  $\text{cm}^3$  of liquid octane would provide,  
 $48.4 \times 0.7 = 33.9 \text{ kJ cm}^{-3}$

Hydrogen (120 kJ g<sup>-1</sup>) and ethanol (30 kJ g<sup>-1</sup>) are suggested as future alternatives to fossil fuels.

Water provides a massive reserve of hydrogen. Research is going ahead to find *economic* methods of separating water into its elements. Spain, for example, has a research power plant (Hydrosol II) which uses sunlight to provide the energy necessary to sustain a chemical reaction in which water is split into hydrogen and oxygen. The chemical reactions, using special metal oxides, operate at about 1500 °C.



The power plant can produce about 3000 g of hydrogen an hour.

[www.hydrosol-project.org](http://www.hydrosol-project.org)

Ethanol can be obtained from vegetable matter by the process of *fermentation* and *distillation*. The vegetable matter, which provides starch for the fermentation, is a renewable resource. However, it is debatable whether sufficient vegetable matter could be produced to satisfy and sustain the demand for ethanol fuel. Ethanol produced in this way is referred to as a biofuel. Brazil produces and makes use of large quantities of ethanol as fuel for the internal combustion engine.

Hydrogen and ethanol are cleaner fuels than the fossil fuels because there is little or no contamination with sulphur; they do not produce the acidic gas sulphur dioxide when burnt. Furthermore, hydrogen fuel does not contribute to the atmospheric carbon dioxide and global

## The Alkenes

Homologous series:

Name	Molecular formula	Structural formula	Boiling point °C
Ethene	C <sub>2</sub> H <sub>4</sub>	CH <sub>2</sub> =CH <sub>2</sub>	-104
Propene	C <sub>3</sub> H <sub>6</sub>	CH <sub>3</sub> CH=CH <sub>2</sub>	-48
But-1-ene	C <sub>4</sub> H <sub>8</sub>	CH <sub>3</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	-6
But-2-ene	C <sub>4</sub> H <sub>8</sub>	CH <sub>3</sub> CH=CHCH <sub>3</sub>	2
Pent-1-ene	C <sub>5</sub> H <sub>10</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	30
Pent-2-ene	C <sub>5</sub> H <sub>10</sub>	CH <sub>3</sub> CH=CHCH <sub>2</sub> CH <sub>3</sub>	37.5

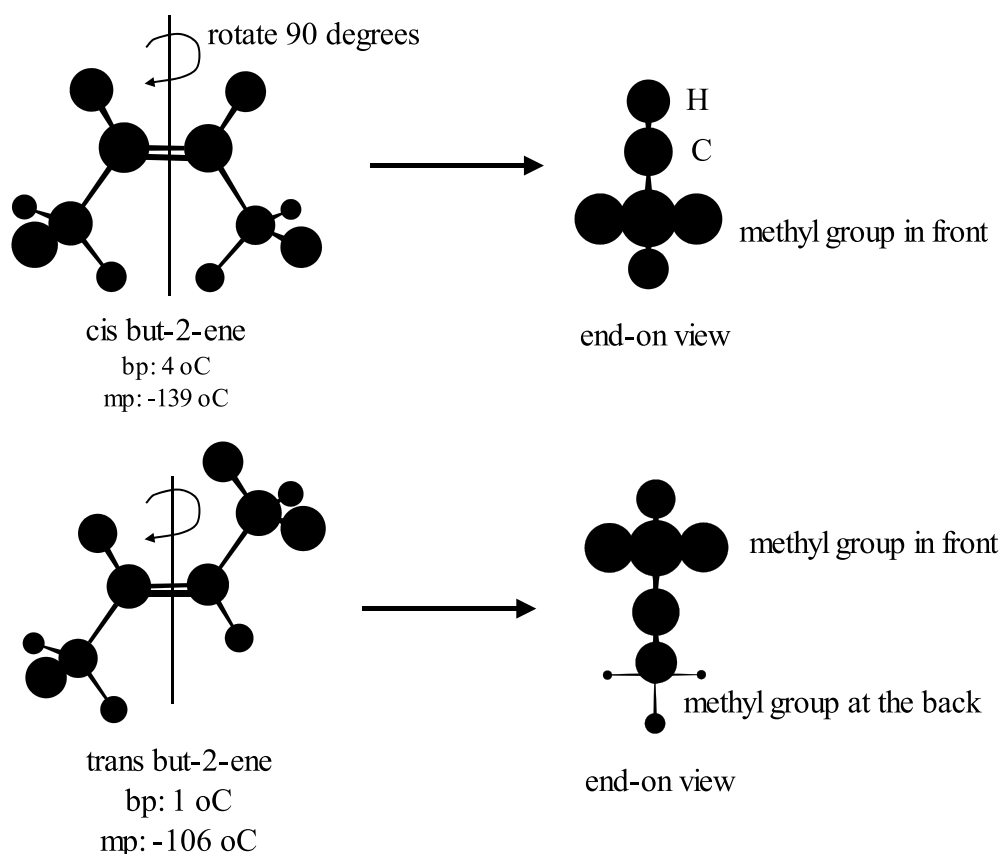
Boiling points increase with increase in carbon chain length because the number of electrons, associated with the carbon chains, is increasing and as a result the van der Waal forces of attraction between molecules increase.

## Geometrical isomers:

The structure at a carbon-carbon double bond is *planar*.

Also, there is *restricted rotation about the double bond*.

If each of the doubly bonded carbon atoms are attached to different groups, the molecule will exist in two geometrical forms which will have different physical properties (and in some cases slightly different chemical properties).

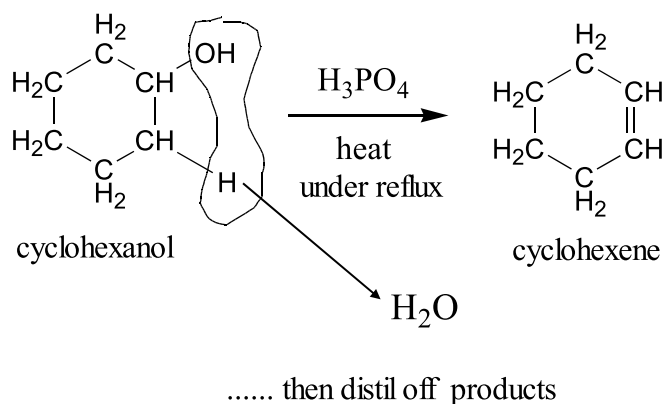


## Sources of alkenes

**On a large scale** alkenes are made from the **naphtha fraction** of crude oil. Naphtha vapour is mixed with steam and heated to about 800°C. Under these conditions, the alkane molecules, which make up the naphtha, fragment and lose hydrogen forming a mixture of alkenes. The process is called **cracking**. The alkene mixture is separated by *fractional distillation*.

**On a small scale**, in the lab, alkenes are often made by **dehydrating alcohols** by heating with phosphoric acid.

eg,

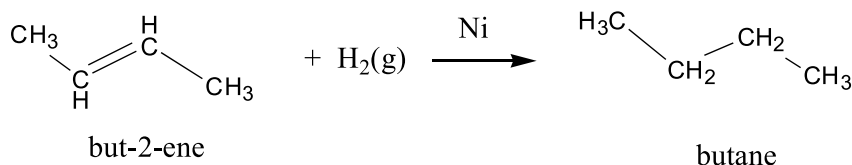


reflux .....then.....distillation

## The typical reactions of alkenes are addition reactions

eg,

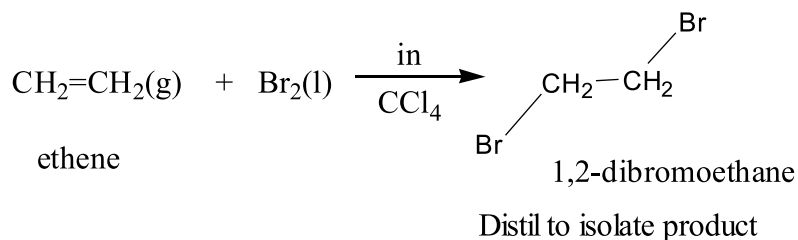
### Hydrogenation



*addition reaction*  
— just one product

Hydrogenation is used commercially to *harden* vegetable oils and produce **margarine**.

### Halogenation.

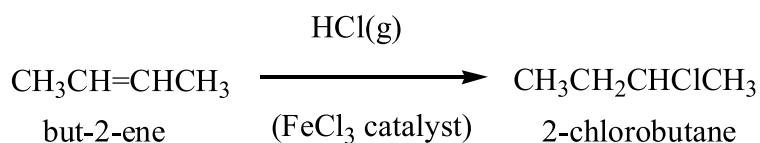
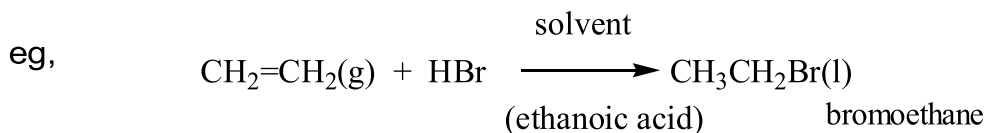


This reaction is initiated by the electrophile,  $\text{Br}^+$  (provided by  $\text{Br}_2$ ). It is an example of **electrophilic addition**.

**Test:** Alkenes *decolourise* solutions of bromine.

## Hydrohalogenation

Alkenes undergo addition reactions with hydrogen halides (*halogen acids*, HX).

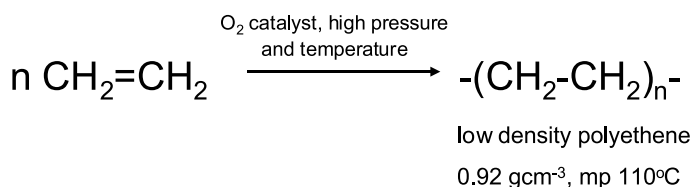
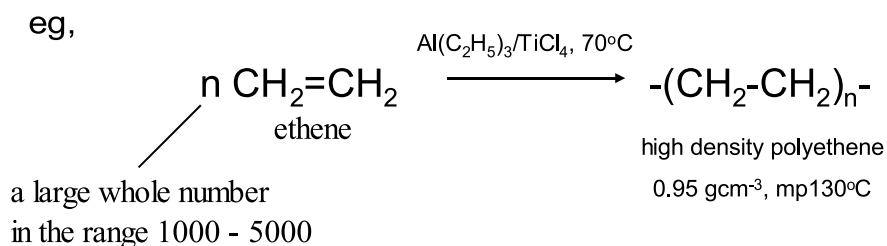


The electrophile,  $\text{H}^+$ , initiates the reaction. Halide ion,  $\text{X}^-$ , completes the reaction. The reaction is another example of **electrophilic addition**.

Order of reactivity with alkene:  
 $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$   
 most reactive

## Polymerisation

In the presence of suitable catalysts alkene molecules will join together forming long chains; the process is called, ***polymerisation***.



$\text{-CH}_2\text{-CH}_2\text{-}$  is known as the ***repeating unit***

### Polymer applications:

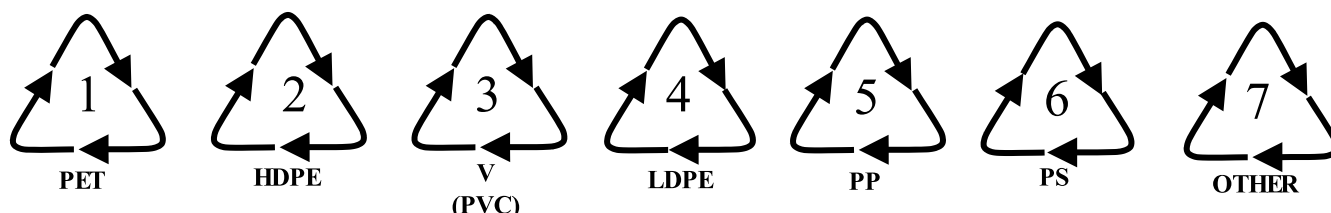
**Polyethene ( $-\text{CH}_2-\text{CH}_2-$ )<sub>n</sub> is used to make plastic bags, sheets and pipes.**

**Polychloroethene ( $-\text{CH}_2-\text{CHCl}-$ )<sub>n</sub> (also referred to as PVC) is used to make gutterings, water tanks, pipes, floor tiles, hose pipes, insulation for electric cables and many household items.**

**Polytetrafluoroethene (PTFE) ( $-\text{CF}_2-\text{CF}_2-$ )<sub>n</sub> has a high softening point (about 330°C) and is used to make heat resistant non-stick surfaces, insulation for electric cables, bearings and chemical plant.**

**Polypropene ( $-\text{CH}(\text{CH}_3)-\text{CH}_2-$ )<sub>n</sub> is a fairly rigid plastic and is used to make car components, household goods, ropes, fishing nets and fibres for carpets.**

If you look on a plastic container (usually on the base of the container) often there is a symbol which tells you what the container is made of. They look like this:



PET: polyethylene terephthalate, HDPE: high density polyethylene, PVC: polyvinyl chloride, LDPE: low density polyethylene, PP: polypropylene, PS: polystyrene, OTHER: eg, nylon, polycarbonates, polyurethane.

An increasing amount of effort is going into devising ways and means of recycling plastics. This is to avoid or reduce our reliance on natural gas and oil which are the raw materials for the manufacture of virgin plastics. In order for recycling to be effective the plastics must be identified so that they can be separated and processed appropriately. This is why the above identifying marks are particularly important.

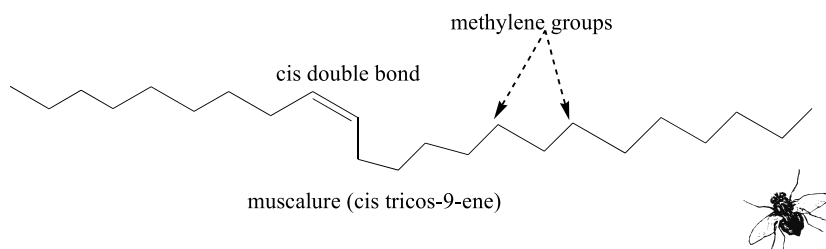
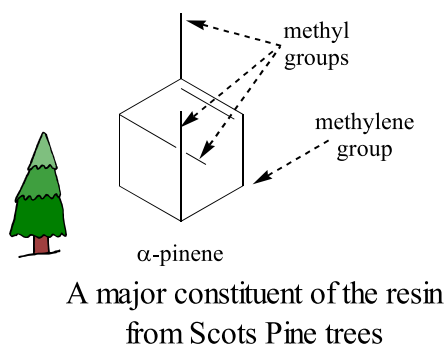
At the present time PET & HDPE plastics are recycled in largest quantities.

A number of websites provide useful information about plastics, eg, [www.modernplastics.com](http://www.modernplastics.com), [www.pacia.org.au](http://www.pacia.org.au), [www.plastics.org.nz](http://www.plastics.org.nz), [www.wasteonline.org.uk/resources/Information sheets/Plastics.htm](http://www.wasteonline.org.uk/resources/Information sheets/Plastics.htm).

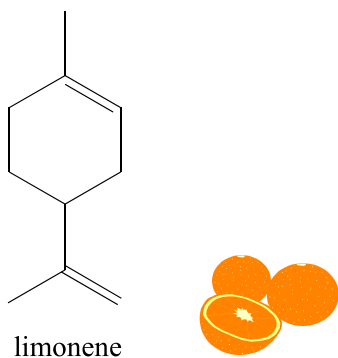
## Unsaturated compounds in nature

Unsaturated hydrocarbons containing the carbon-carbon double bond are widely distributed in nature.

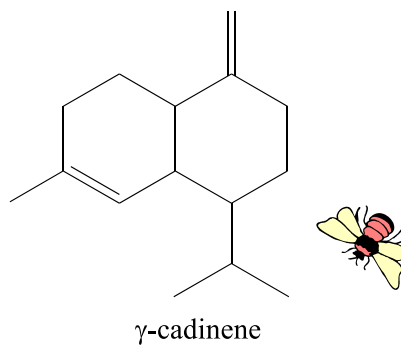
eg,



The sex attractant of the female common house fly (*Musca domestica*)



The major constituent of the oil from orange peel



A constituent of the fragrance of ophrys orchids (found in Mediterranean countries). It is highly attractive to the pollinating bees.

The above formulae are **symbols** for the molecules. Simply as a matter of convenience, representations like these are often used as shorthand to depict complex molecules.



# Theme Eleven

## Organic Chemistry II

### Halogenoalkanes

Halogenoalkanes are organic compounds in which halogen is covalently bonded, directly, to carbon.

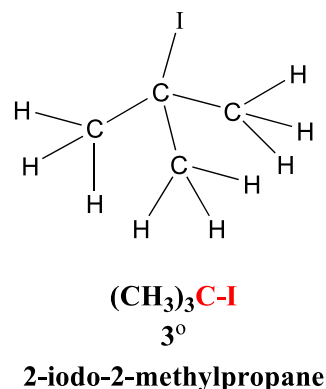
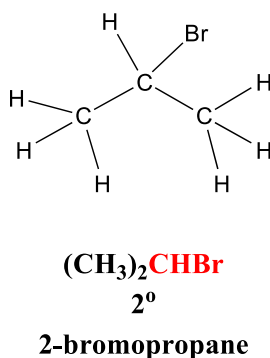
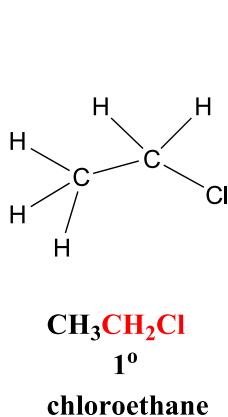
The simplest, the *monohalogenoalkanes*, form a homologous series and have the general formula,



where X represents a halogen atom.

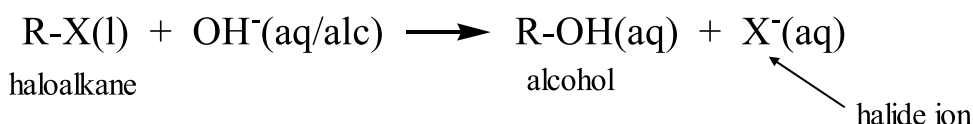
eg,	Name	Formula	Bp °C
	chloromethane	$\text{CH}_3\text{Cl}$	-24
	chloroethane	$\text{CH}_3\text{CH}_2\text{Cl}$	13
	1-chloropropane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	47
	1-chlorobutane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	79

Some examples of primary, secondary and tertiary halogenoalkanes:

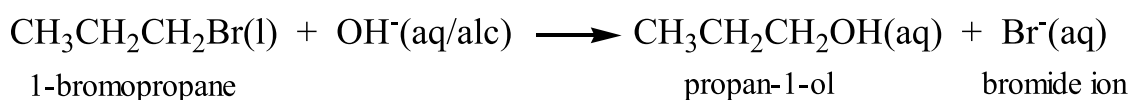


## Chemical properties of Halogenoalkanes (haloalkanes)

### Hydrolysis



eg,



This is an example of **nucleophilic substitution**. The halogen is replaced by hydroxyl group which is provided by water or an alkali metal hydroxide dissolved in water; in pure water the reaction is slow.

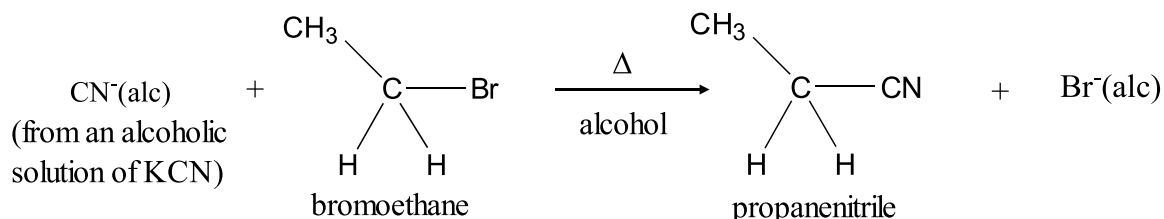
To ensure a satisfactory rate of hydrolysis and yield of hydrolysis product:

1. Heat the reaction mixture.
2. Provide adequate hydroxide concentration by using an aqueous-alcoholic solution of sodium or potassium hydroxide (rather than just water). Aqueous-alcoholic solvent is usually employed to ensure miscibility and good contact between reactants.
3. Use iodo- or bromo-alkane since they are generally easier to hydrolyse than chloroalkanes (the C-Cl bond is a strong bond and more difficult to break during hydrolysis).
4. As a general rule, tertiary haloalkanes are easier to hydrolyse than secondary and secondary easier to hydrolyse than primary.

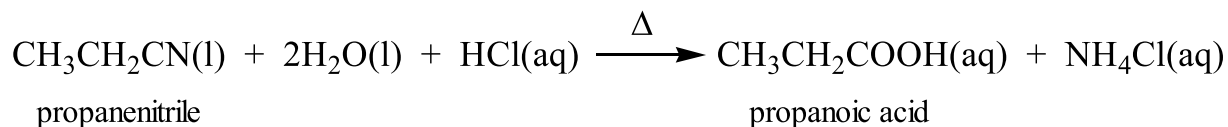
The hydrolysis reaction can be used to test for haloalkanes since the halide ion can be readily detected in the reaction mixture by acidifying with dilute nitric acid and adding silver nitrate solution. A white precipitate of silver chloride is formed.

### Reaction with Potassium cyanide

eg,



Nitriles are synthetically useful since they are readily hydrolysed to **carboxylic acids**.  
eg,



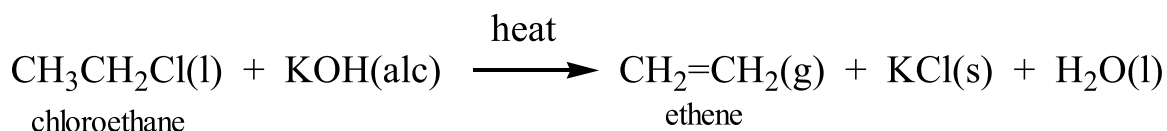
## Stepping up a homologous series

These reactions enable you to introduce a carbon atom into an existing carbon chain. The nitrile group contains the extra carbon atom and once introduced it can be converted into a number of different functional groups. As the above equation shows, it is easily converted to the carboxyl group. It can also be reduced to the primary amine group  $-\text{CH}_2\text{NH}_2$ .

## Reaction with an alcoholic solution of Potassium Hydroxide.

When heated with this reagent, haloalkanes undergo **elimination**. The haloalkanes lose the elements of the corresponding hydrogen halide.

eg,



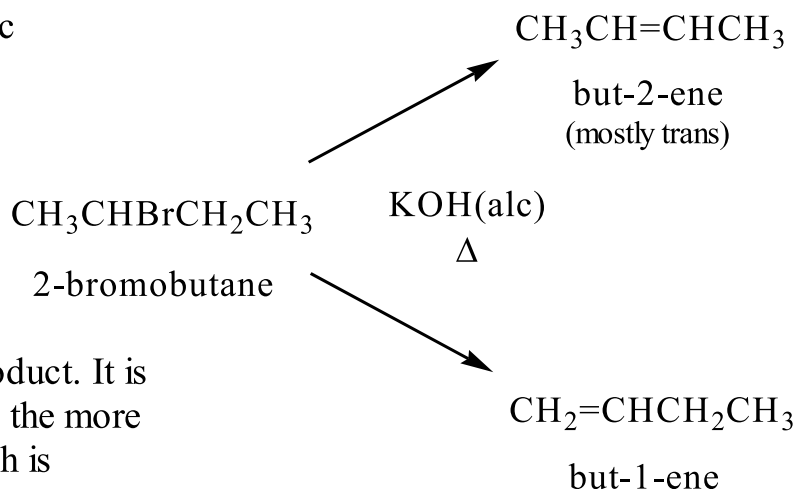
In this example, chloroethane has lost the elements of HCl and has been converted to the corresponding alkene. We say that chloroethane has undergone *elimination* and HCl has been **eliminated**.

**Note:** Since the reaction mixture contains hydroxide ion some *substitution* will occur alongside elimination. However, higher temperatures and higher hydroxide concentrations, in alcohol solution, favour elimination over substitution.

Also, secondary and tertiary haloalkanes undergo elimination more readily than primary haloalkanes.

Some haloalkanes produce a number of alkenes when heated with an alcoholic solution of KOH.

eg,



In this case but-2-ene is the major product. It is more stable than but-1-ene. Also, it is the more stable *trans* isomer of but-2-ene which is formed preferentially.

As a general rule, the more highly substituted the alkene is, at the double bond, the more stable it is. This was first observed by the Russian chemist, Alexander.N.Zaitsev (1841-1910). In English literature his name is often spelt Saytzeff.

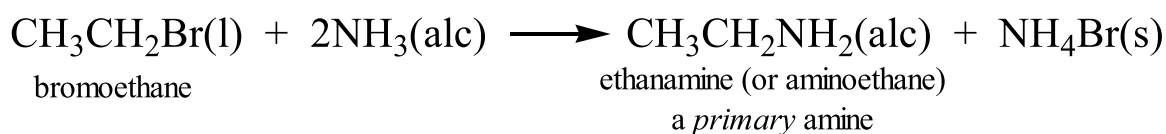
[http://en.wikipedia.org/wiki/Alexander\\_Mikhailovich\\_Zaitsev](http://en.wikipedia.org/wiki/Alexander_Mikhailovich_Zaitsev)

[http://en.wikipedia.org/wiki/Zaitsev's\\_rule](http://en.wikipedia.org/wiki/Zaitsev's_rule)

## Reaction with Ammonia

Heat the haloalkane with ammonia, dissolved in alcohol, in a sealed glass tube.

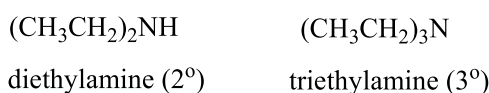
eg,



Two moles of ammonia, rather than one, is required to ensure that liberated  $\text{H}^+$  is neutralised as  $\text{NH}_4^+$  (ie,  $\text{H}^+ + \text{NH}_3 \longrightarrow \text{NH}_4^+$ ).

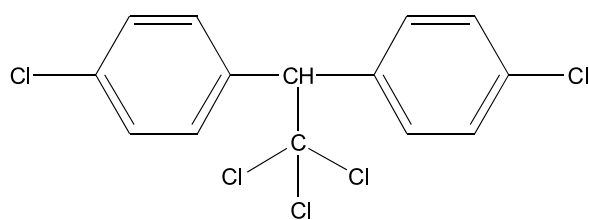
The reaction is an example of nucleophilic substitution where the nucleophile is  $\text{NH}_3$  (the lone pair on the nitrogen are provided to form the new covalent bond)

To maximise the yield of primary amine and avoid the formation of *secondary* and *tertiary* amines, an excess of ammonia should be used.



Chloroalkanes (and haloalkanes generally) are useful intermediates in the manufacture of anaesthetics (eg,  $\text{C}_2\text{H}_5\text{Cl}$ ), silicone polymers (used as sealants) and various herbicides and pesticides. Chlorofluorocarbons have been used as refrigerants, blowing & degreasing agents.

The C-Cl bond is quite strong and it not only provides herbicides and pesticides with the desired biological activity but also enhances their active life in the environment. The downside of this is that some of these chemicals, like the pesticide DDT, remain in the environment for long periods and get into the food chain causing harmful effects.



*dichlorodiphenyltrichloroethane (DDT)*

## Alcohols

These are aliphatic hydroxy compounds. The simplest have the general formula,  $\text{C}_n\text{H}_{2n+1}\text{OH}$ . They are sometimes represented,  $\text{R-OH}$  where R is an alkyl group such as,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$ ,  $\text{C}_4\text{H}_9$ , etc.

The alcohols are classified as primary ( $1^\circ$ ), secondary ( $2^\circ$ ) and tertiary ( $3^\circ$ ).

Class of alcohol	General Formula	Example
primary	$\begin{array}{c} \text{R} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$
secondary	$\begin{array}{c} \text{R} \\   \\ \text{R}'-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$
tertiary	$\begin{array}{c} \text{R} \\   \\ \text{R}'-\text{C}-\text{OH} \\   \\ \text{R}'' \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{OH} \\   \\ \text{CH}_3 \end{array}$

Name	Formula	Boiling Point (°C)
Methanol	CH <sub>3</sub> OH	65
Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	78
Propan-1-ol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	97
Butan-1-ol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH	117

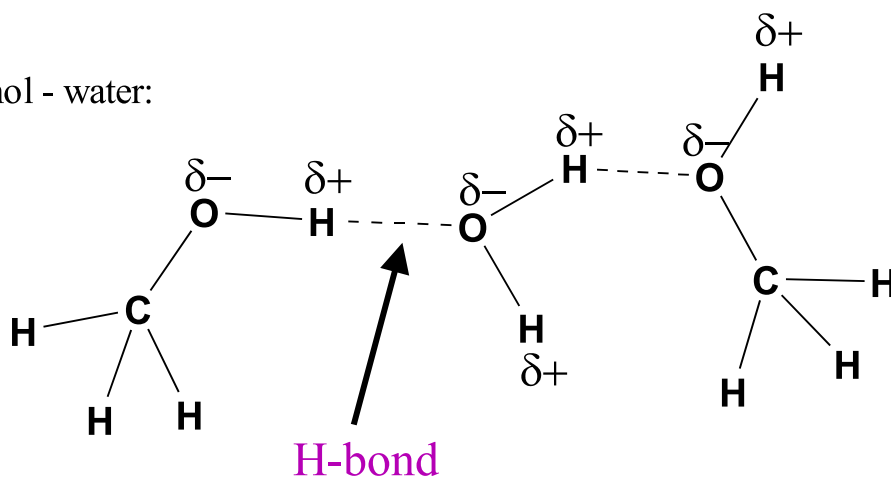
Methanol and ethanol are freely soluble in water.

Solubility *decreases* down the group.

Hydrogen bonding between alcohol and water molecules enhances solubility.

Increase in bp with increase in chain length and van der Waal attractive forces.

eg, methanol - water:

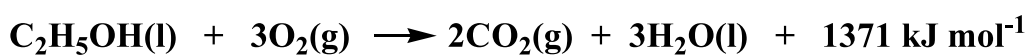


## Oxidation.

### (i) Combustion:

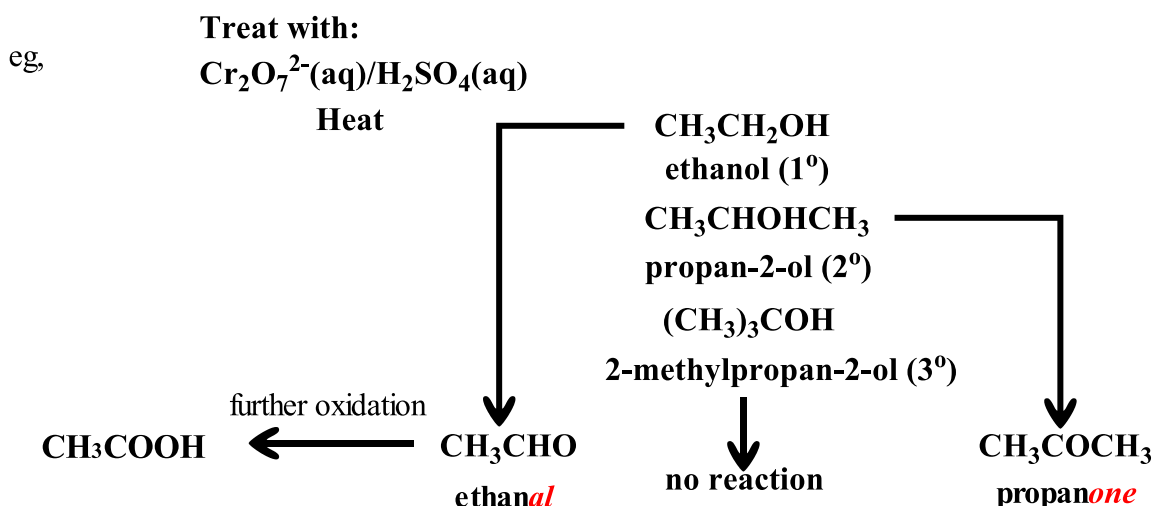
**Burn readily in oxygen (or air). Burn with a clean flame.**

eg,



## (ii) Potassium dichromate

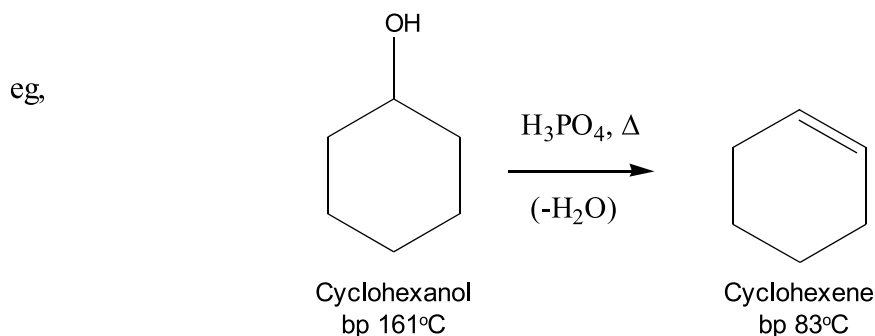
Primary and secondary alcohols are oxidised by warming with a solution of potassium dichromate acidified with dilute sulphuric acid. Primary alcohols form *aldehydes* and secondary alcohols form *ketones*. Aldehydes undergo further oxidation to *carboxylic acids* ( $RCOOH$ ). Tertiary alcohols do not react.



**Note:** the oxidations are accompanied by a colour change. The dichromate reagent is **orange** due hydrated dichromate ion and the final reaction mixture is **green** due to hydrated chromium (III) ion. The reaction can be used to test for primary and secondary alcohols. Furthermore, primary and secondary alcohols can be distinguished by distilling off a small amount of the carbonyl compound and testing with Tollens reagent (an ammoniacal solution of silver nitrate). This gives the *silver mirror* effect with aldehydes. Ketones do not react with Tollens reagent.

## Dehydration

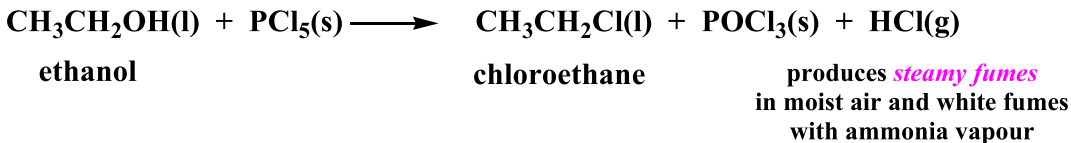
Alcohols lose the elements of water when heated with concentrated sulphuric acid or with concentrated phosphoric acid and form alkenes. The alcohol is said to be *dehydrated*.



# Halogenation

(i) **Chlorination:** Primary and secondary alcohols react with phosphorus pentachloride forming chloroalkanes.

eg,

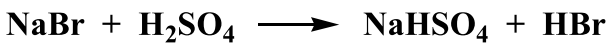


$\text{PCl}_5$  is often used to show the presence of the OH group in alcohols and in other compounds such as carboxylic acids.

Tertiary alcohols react with  $\text{PCl}_5$  but give much poorer yields.

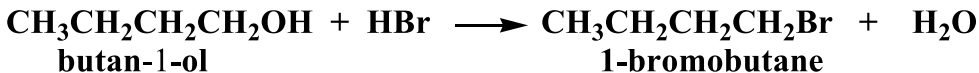
(ii) **Bromination** can be achieved by reaction with hydrogen bromide. This is produced *insitu* by reaction between sodium bromide and concentrated sulphuric acid.

ie,



(some bromine is formed due to the oxidation of HBr by concentrated sulphuric acid)

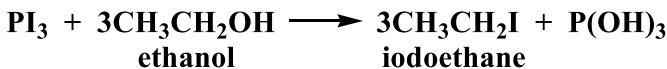
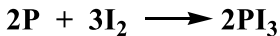
Then,



Since hot sulphuric acid is being used, some dehydration to alkene also occurs.

(iii) **Iodination** may be achieved by heating the alcohol with red phosphorus and iodine. The elements combine to give phosphorus tri-iodide and this reacts with the alcohol to give iodoalkane.

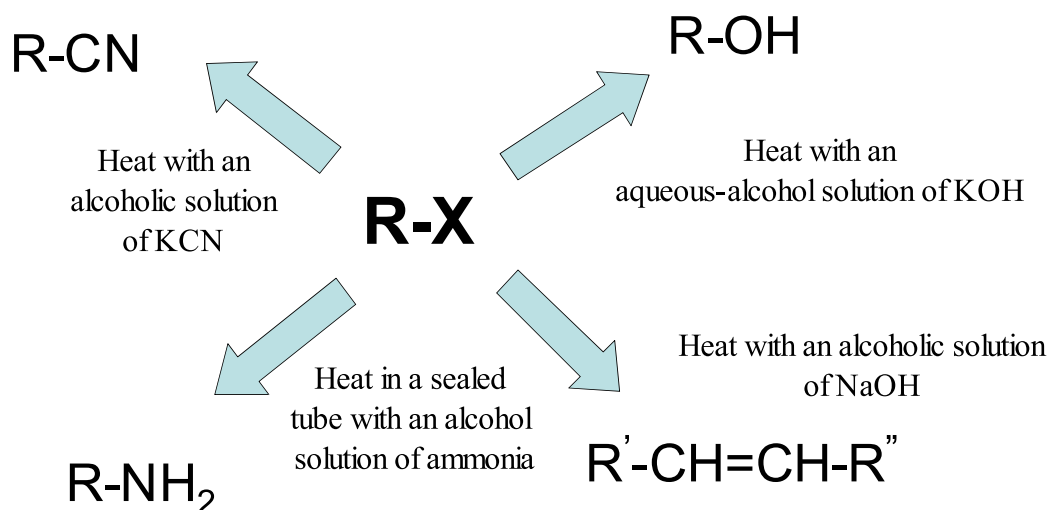
eg,



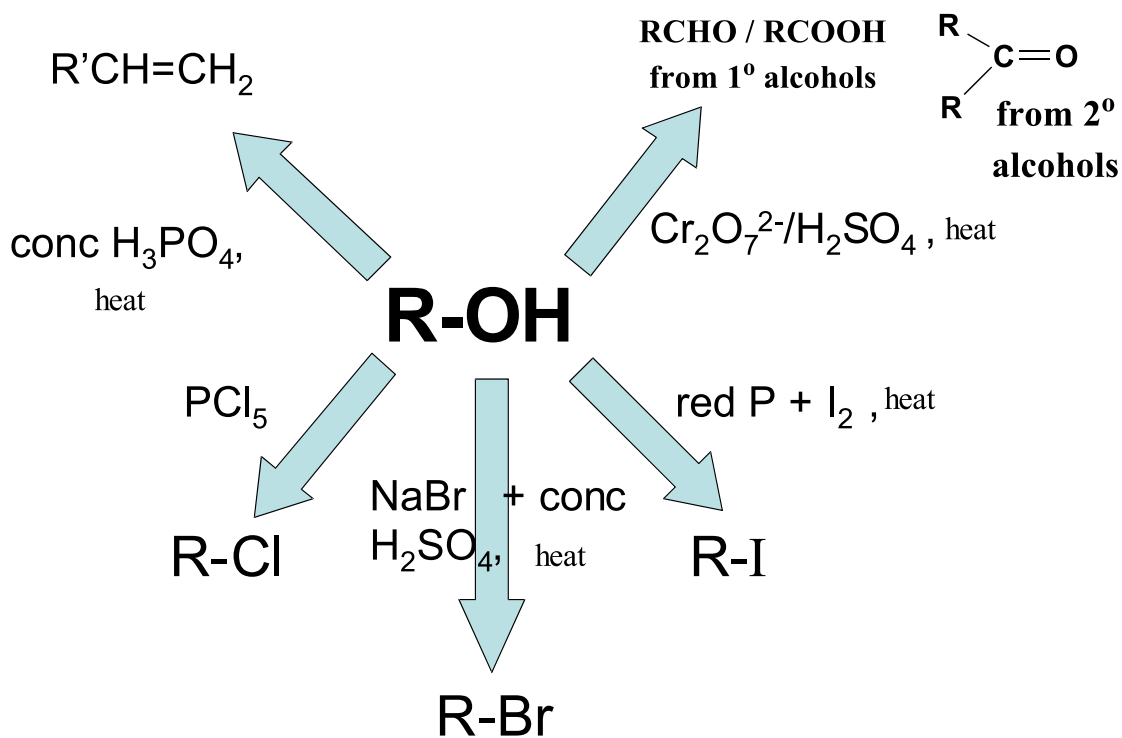


# Summaries:

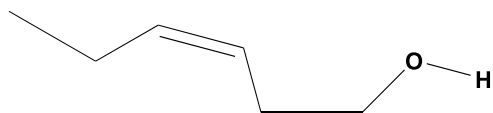
## Halogenoalkanes



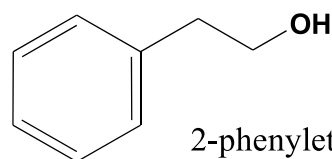
## Alcohols



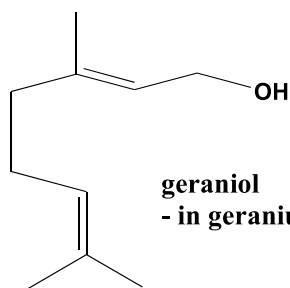
## Naturally occurring Hydroxy & Halogen containing organic compounds



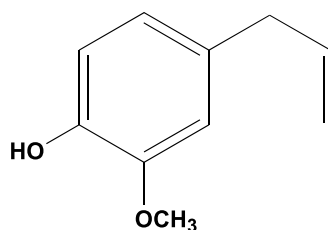
**cis-hex-3-en-1-ol**  
(leaf alcohol - in many grasses, green leaves & herbs)



**2-phenylethanol**  
- present in rose oil



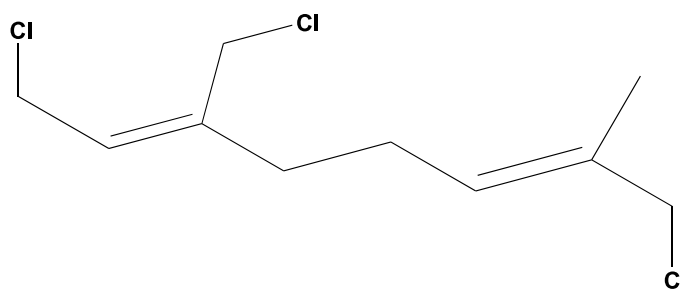
**geraniol**  
- in geranium oil



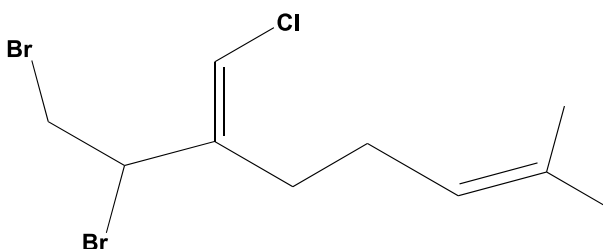
**eugenol - in clove oil**  
(this is an aromatic hydroxy compound, a *phenol*)

Both of these compounds have been isolated from the red alga, *chondrococcus hornemannii*, found on the Great Barrier Reef, Australia.

Marine organisms provide rich sources of halogenated organic compounds.



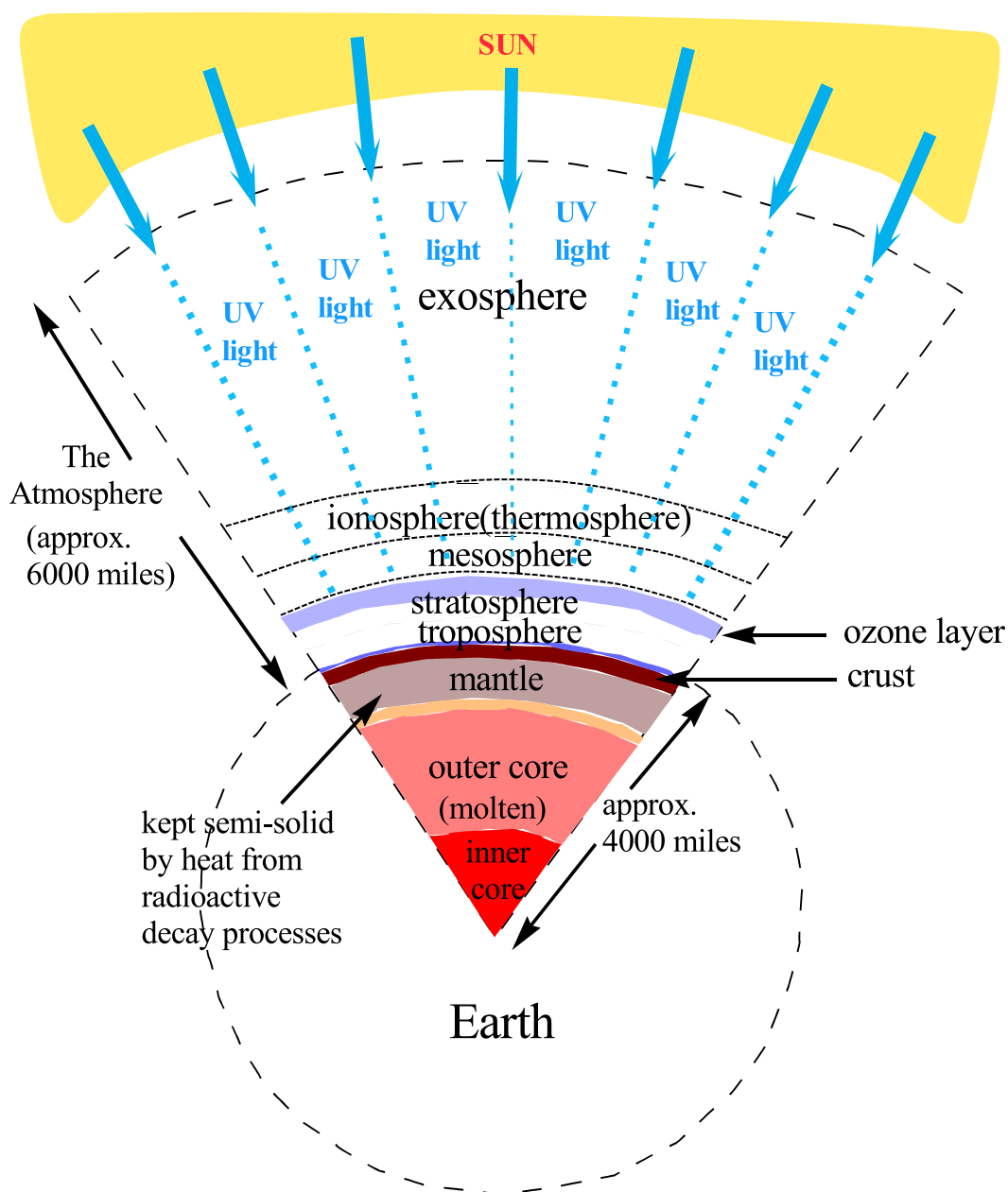
**1,8-dichloro-3-chloromethyl-7-methylocta-2,6-diene**



**1,2-dibromo-3-chloromethylene-7-methyloct-6-ene**

## CFC's and the Ozone Layer

When we speak of the *ozone layer* we are normally referring to the ozone in the stratosphere (see diagram below - not to scale).



**SUN**

Ozone in the atmosphere, particularly the upper atmosphere (stratosphere), helps protect us from the harmful effects of ultra-violet light from the sun. It absorbs ultra-violet light and in so doing it undergoes photodissociation & is converted into oxygen molecules and oxygen atoms.

$$\text{O}_3(\text{g}) + h\nu \rightarrow \text{O}_2(\text{g}) + \text{O}(\text{g})$$

The oxygen atoms are reactive and readily combine with more ozone giving oxygen molecules.

$$\text{O}(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{O}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta H = -390 \text{ kJ mol}^{-1}$$

Ozone is replenished by the reverse of the ozone photodissociation reaction.

$$\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{O}_3(\text{g}) \quad \Delta H = -100 \text{ kJ mol}^{-1}$$

Oxygen atoms are provided in the stratosphere by the photodissociation of ozone & oxygen molecules.

$$\text{O}_2(\text{g}) + h\nu \rightarrow \text{O}(\text{g}) + \text{O}(\text{g})$$

Under natural conditions the reactions occurring in the stratosphere would achieve a steady state and the concentration of ozone would remain constant. However, in recent times the ozone concentration has shown a steady decline as a result of the introduction, into the atmosphere, of man-made molecules such as halogen containing organic compounds. The chlorofluorocarbons (CFC's) are the major offenders because of their characteristically high stabilities. It is estimated that CFC molecules have a life time of 20 to 100 years in the atmosphere.

**Less ozone in the stratosphere means more harmful UV light reaching the troposphere and the earth's surface.**

CFC's were introduced as refrigerants, degreasing solvents and blowing agents from 1930 onwards. Thomas Midgley performed the initial research and developed dichlorodifluoromethane as a replacement for the toxic ammonia and sulphur dioxide refrigerants. By 1975 it became clear that CFC's had a harmful effect on the ozone layer and following the Montreal Protocol (1987) the production of CFC's should cease in all countries by 2010. When the CFC's reach the stratosphere they undergo photodissociation resulting in the formation of Cl free radicals. Each one of these can destroy 100 000 ozone molecules! The critical reactions are:

$$\text{Cl}\cdot(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{ClO}\cdot + \text{O}_2(\text{g})$$

$$\text{ClO}\cdot(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{Cl}\cdot(\text{g}) + 2\text{O}_2(\text{g}) \text{ etc}$$

The Cl free radicals react rapidly with ozone molecules and via chlorine oxide (ClO), they are continually regenerated. Research is in progress to find ozone friendly alternatives to the CFC's and to find ways of reducing the damage already caused to the ozone layer.

The highest concentrations of ozone (O<sub>3</sub>) are found in this layer (about 0.001% by volume).

You need to be aware that numerous reactions occur in the atmosphere. Many are natural in origin and have been occurring for millions of years. However, the activities of man are adding to these atmospheric reactions with harmful long term consequences. Reactions involving halogen containing compounds and nitrogen oxides (from the use of fertilizers, the internal combustion engine and heavy industry) are important examples. An additional problem is the accumulation of waste gases and vapours (such as carbon dioxide, methane and halogen compounds) in the troposphere which give rise to the **greenhouse effect**. These waste gases absorb (& trap) infra red radiation increasing the heat content of the lower atmosphere & preventing it escaping normally into the outer atmosphere. This gives an abnormal greenhouse effect causing the overall temperature of the earth to increase. The temperature rise, so far, has been small (fractions of a degree) but the consequences are marked. The melting of the polar ice is of major concern.

**Earth**

dichlorodifluoromethane  
(a CFC)

## Using Infra-red light to identify functional groups in molecules

### Infra-red

The chemical bonds, holding atoms together within molecules, behave in many respects like simple metal springs.

Like springs they will allow a certain amount of movement both longitudinally and transversely.

The former is referred to as **stretching vibration** and the latter as **bending vibration**.

The energy required to cause these bond vibrations is provided by electromagnetic radiation in the **infra-red region** of the spectrum.

Most of the covalent bonds, found in organic molecules, absorb infra-red radiation in the wavelength range  $2.5 \times 10^{-4}$  cm to  $25 \times 10^{-4}$  cm

Since *wavenumber* ( $\bar{\nu}$ ) is directly proportional to the energy of the radiation, it is common practice to translate wavelengths into **wavenumbers** where the wavenumber is simply the reciprocal of wavelength.

Then,  $2.5 \times 10^{-4}$  cm wavelength is equivalent to  $4000 \text{ cm}^{-1}$  wavenumber and  $25 \times 10^{-4}$  cm wavelength is equivalent to  $400 \text{ cm}^{-1}$  wavenumber.

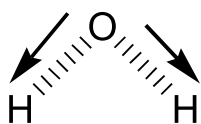
$4000 \text{ cm}^{-1}$   
high energy



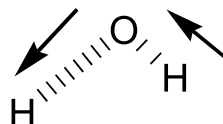
$400 \text{ cm}^{-1}$   
low energy

Strong covalent bonds require high energy infra-red radiation to cause them to undergo stretching vibrations.

For example, the hydrogen-oxygen bonds in the water molecule show stretching vibrations at high wavenumber values.



symmetrical  
stretch  
( $3657 \text{ cm}^{-1}$ )

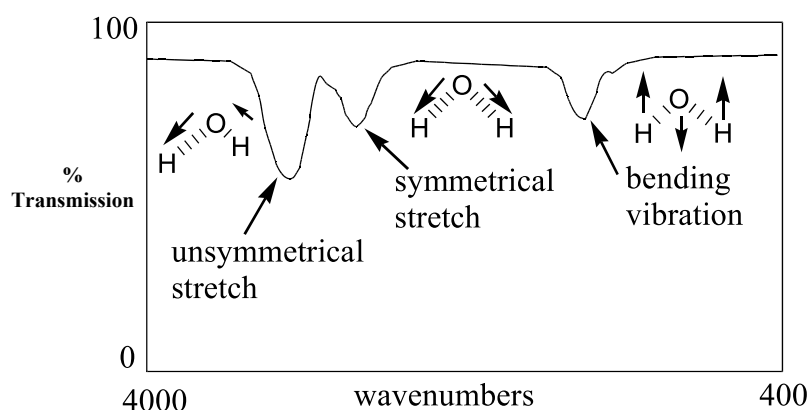
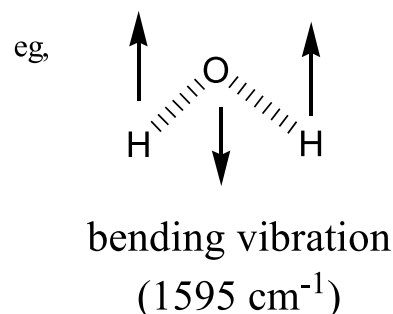


unsymmetrical  
stretch  
( $3756 \text{ cm}^{-1}$ )

**Bending vibrations** occur at lower wavenumber values.

Commercial instruments are available, known as infra-red spectrophotometers, which can expose molecular substances to infra-red light in the  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  wavenumber range and measure the amount of light absorbed by the sample in this range. The resulting print out is known as an *infra-red spectrum*.

The infra-red spectrum of water shows absorption peaks corresponding to the various bond vibrations.



Many thousands of organic compounds have been examined using infra-red spectrophotometers and tables have been drawn up listing all the major structural features of molecules and the corresponding wavenumber values.

eg,

Bond/Group	Wavenumber ( $\text{cm}^{-1}$ )	Bond/Group	Wavenumber ( $\text{cm}^{-1}$ )
OH stretch	3650-3500	non-conjugated C=C stretch	1650 (subtract 20 $\text{cm}^{-1}$ if conjugated to another C=C)
NH stretch	3400-3200	carboxylate asym stretch ( $-\text{COO}-$ )	1550-1610
alkyne C-H stretch	3300	benzene ring	1500 & 1600
alkene C-H stretch	3000-3100	CH scissoring	1500-1400
aromatic C-H stretch	3020-3100	scissoring	1375
aliphatic C-H stretch	2800-3000	C-O-C intense bands	1250-1000
aldehyde C-H stretch	2700	trans H-C=C-H	975
carboxylic acid OH (broad, ill defined peak)	about 3000		900-925
nitriles	2250	C-Cl	725-850
alkyne CH stretch	2100	phenyl group	700
saturated ester C=O stretch	1735*	* If the carbonyl group is conjugated, subtract $20\text{ cm}^{-1}$ ; if the carbonyl group is doubly conjugated, subtract $40 - 50\text{ cm}^{-1}$ .	
saturated ketone C=O stretch	1700*		
saturated aldehyde C=O stretch	1710*		
saturated acid C=O stretch	1700*		
saturated amide C=O stretch	1690-1650		

The value of this information is that by obtaining the infra-red spectrum of an unknown compound and noting the wavenumber values of the major peaks, it is possible to identify functional groups and various other structural features relating to its molecular structure.

Particularly useful and easily recognised absorptions include the hydroxyl (OH) which is broad and occurs at about  $3500\text{ cm}^{-1}$ , the amino group ( $\text{NH}_2$ ) which occurs in the same region as the hydroxyl group but gives a somewhat weaker, sharper, absorption usually observed as a doublet, the alkyne C-H stretch which is usually an intense, fairly sharp, peak at  $3300\text{ cm}^{-1}$ , saturated and unsaturated C-H stretching just below and just above  $3000\text{ cm}^{-1}$  and the carbonyl absorption which is nearly always intense and occurs in the region of  $1700\text{ cm}^{-1}$ . These bond vibrations are sometimes referred to as *localised vibrations* to distinguish them from the more generalised vibrations involving the whole molecule. The localised vibrations usually occur in the high energy region of the spectrum whereas whole molecule vibrations occur below  $1500\text{ cm}^{-1}$  in the low energy, or *fingerprint region*.

